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PROCEEDINGS

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on Chemical Spills

Huitième colloque
technique sur les
déversements de produits
chimiques

June 10-11, 1991
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A NATURAL RESOURCE DAMAGE ASSESSMENT MODEL AND GEOGRAPHICAL INFORMATION SYSTEM FOR THE GREAT LAKES

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ABSTRACT

A dynamic model of the physical transport, biological effects, and economic damages resulting from releases of oil and other hazardous materials is presented. The model has been applied to the Great Lakes and connecting rivers, but may be readily adapted to other freshwater as well as marine environments. A coupled geographical information system (GIS) allows automated gridded representation of complex coastal boundaries, variable bathymetry, shoreline types, and biological habitats. The model incorporates flows in rivers, and a wind-driven hydrodynamic model for lakes. Both the physical and biological models are three-dimensional. The model is implemented on a personal computer, and comes with a VGA graphical user interface. Following public review, the model system will become a formal part of the U.S. regulatory framework. The model is programmed in a modular and generic fashion, to facilitate transportability and application to new areas.

INTRODUCTION

The United States Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) allows the Federal or a state government, as trustee of affected natural resources, to claim compensation for spill-related damages to those resources, as well as the reasonable cost of conducting a natural resource damage assessment. Such assessments may be conducted using either a Type A (simple) or Type B (complex) methodology, the simpler methodology being indicated when a refined, site-specific Type B assessment is not warranted in a cost/benefit sense. The first Type A methodology (Reed et al., 1989) was developed for the coastal and marine environments (CME), and was published in the Federal Register on March 20, 1987 (52 FR 9042). The methodology described herein is applicable to the Great Lakes environments (GLE), including connecting channels and rivers.

Like the CME model, the GLE model is comprised of a series of linked submodels and data bases (Figure 1). The GLE model is supported by a geographical information system which supplies spatially gridded environmental and biotic information to the dynamic physical fates and biological submodels. The user is required to supply the name of the spilled substance, the amount spilled, the duration of the release, the time and date of release start, a wind time series, the latitude and longitude of release point, and to what extent cleanup of the spill was carried out. The GIS then supplies bathymetry, shoreline types, ecological habitat, ice cover, river currents, and climatological lake currents. Lake currents are computed dynamically by the hydrodynamic model for the duration of the wind time series supplied by the User. These parameters vary spatially within the model. Ice cover, currents, water temperature, and thermocline depth also vary temporally, and are updated periodically by the GIS.

The wind time series is supplied as an external file by the user. New wind speeds and directions are required for every 3 to 12 hours, beginning 24 hours before the start of the release, and continuing for the duration of the release, or until no surface slick remains. Upon reaching the end of this file, the model uses typical climatological values from the GIS data base.

The physical fates model then computes the dynamic distribution of the spilled substance in the lake or channel environment. Computations continue until either (a) all environmental exposure levels are below a minimum threshold, or (b) a surface slick or water column concentration above the threshold is advected outside the model domain. Under case (a) above, control is passed to the biological effects model and computations proceed. If one of the conditions under (b) occurs, the model will restart using a larger grid size or an adjacent downstream grid, so that damages may be computed for the active life of the release.

The biological effects model computes (1) direct lethal effects on larvae, juveniles and adult fish, waterfowl, shorebirds, and lower trophic biota; (2) indirect and long term effects involving the eventual loss of fish as a result of lost larvae and juveniles, and birds as a result of lost broods; (3) indirect effects of lost lower trophic biota and non-commercial species through the food web. These effects are computed by dynamic juxtaposition of biotic distributions with the distributions of the spilled substance on the water surface, in the water column, in the sediments, and along the shoreline.

The economic submodel then proceeds to compute damages based on methodologies still to be devised. All damages are then summed to produce a final damage measure in U.S. dollars for the release.

MODEL OVERVIEW

The purpose of the physical fates submodel is to estimate the distribution of a contaminant on the water surface, concentrations in the water column, and in the sediments. The GIS establishes an initial boundary and grid system for a specific application of the NRDAM/GLE. The GIS then supplies parameter values for depth, sediment type, ecological habitat, shoreline type, and ice cover throughout the established domain. The chemical data base supplies chemical parameters required by the submodel. The user is required to supply a wind time series specific to the time and location of the spill. The GIS supplies climatological values for air and water temperatures; these may be overridden by the user.

If the specific gravity of a spilled chemical is less than or equal to that of water, the model employs surface spreading, advection, entrainment, and volatilization algorithms to determine transport and fate at the surface. A contaminant with specific gravity greater than water is modeled by a convective jet algorithm which allows the contaminant plume to reach an equilibrium position in a stratified water column, or to sink to the bottom. In general, some fraction of any contaminant spilled will exist in both the water column and the sediments. In the water column, horizontal and vertical advection and dispersion are simulated by random walk procedures. Partitioning between the particulate adsorbed and dissolved states is calculated based on linear equilibrium theory. The contaminant fraction that is adsorbed to suspended particulate matter is assumed to settle at a rate typical for the lacustrine environment. Contaminants at the bottom are mixed into the underlying sediments according to a simple bioturbation equation.

The physical environment is divided into six general compartments: the atmosphere, the sea surface, the upper and lower water column (as defined by the presence of a thermocline), the lake bottom, and the shoreline. The model distributes a contaminant dynamically within and among these compartments. Only the atmospheric compartment has no physical representation and no linkage to the biological effects submodel.

The model solves the generalized transport equation,

$$\frac{\partial C}{\partial t} + \vec{V} \cdot \vec{\nabla} C = \vec{\nabla} \cdot D \vec{\nabla} C - \sum_{j=1}^{n} r_j C \ . \tag{1}$$

On the water surface and the shoreline, "concentration" C has units of mass per unit area, whereas in the water column the units are as usual mass per unit volume. The terms r_j in Equation (1) are process rates, including

- evaporation from surface slicks,
- spreading of surface slicks,
- deposition from water surface onto coastline,
- entrainment and dissolution into the water column,
- volatilization from water column,
- degradation (surface, water column, shoreline, sediments),
- mass removal by cleanup,
- addition of mass from continuous release,
- dissolution from sediments to water column,
- deposition from water column to sediments.
- removal from coastline to water column.

These process rates result in mass transfers from one model compartment to another.

The biological effects submodel estimates short-term losses (injury) resulting from a spill (i.e., losses at the time of the spill and while toxic concentrations remain in the environment) in terms of direct mortality and biomass not produced because of the loss of food resources. Losses are estimated by species or species group for fish and wildlife (birds and mammals).

The environment is represented by a grid of habitats with each grid codes as to habitat type. The habitat grid matches the fixed (Eulerian) physical grid set up by the physical fates model using the GIS data base. A grouping of habitat grids with the same habitat code constitutes an ecosystem in the biological submodel. Fish, birds, mammals and rates of lower trophic level productivity are assumed constant and evenly distributed across an ecosystem within each of four seasons. Fish, birds and mammals are assumed to move at random within each ecosystem during a single season. Fish eggs and larvae are assumed constant and evenly distributed across each ecosystem within each month of an annual cycle. Planktonic stages are advected with the currents.

Habitats include deepwater, nearshore, and wetland environments in the Great Lakes region. Habitat types are defined by depth, proximity to shoreline(s), bottom type, dominant vegetation type, and the degree to which pollution stress presently exists. The water column may be a single layer or divided into two layers by a thermocline.

The physical fates submodel calculates concentration in three-dimensional space and in time. This information is passed to the biological effects submodel where the portion of exposed organisms in each habitat type which would be killed is calculated from dissolved concentration (in the water or sediment). Mortality is calculated using laboratory acute toxicity test data (LC50, concentration lethal to 50% of test individuals) corrected for temperature and time of exposure, and assuming a log-normal relationship between percent mortality and dissolved concentration. Organisms killed are integrated over space and time and by habitat type to calculate a total short-term kill. This total short-term kill occurs from the time of the spill until the time the containment is dispersed to the point where concentrations are below toxic levels.

Biomass which is not produced as a result of a loss of food resources is estimated using a simple food web model. Lost primary (plant) and secondary (herbivore) production in each habitat is estimated using the EC50, the concentration where growth rate is 50% of the clean control, correcting it for temperature and assuming a log-normal relationship between percent of uninhibited growth rate and concentration.

Potential long-term losses (losses seen after the spill has dissipated) which can result from a spill of a toxic substance include: (1) lost recruitment to a fishery of the larvae and juveniles killed at the time of the spill; (2) lost future growth of the adults killed at the time of the spill; (3) changes in food web structure and, therefore, productivity of specific trophic levels and populations; and (4) chronic effects of sublethal levels of contaminants in tissues or the environment, such as reduced growth rate or loss of reproductive potential. The latter two effects are considered beyond the scope of this model. Thus, the impacts estimated in the biological submodel are the results of acute toxicity and resulting direct effects on long-term productivity and yield; lost recruitment and lost growth. It is assumed that the spill has no indirect (chronic) effects or feedbacks after the spill has dissipated, such as changes in mortality due to density-dependent effects, changes in food web structure and predator-prey relationships, or changes in reproductive potential. The spill impact extends only for the life span of the species considered, and growth, biomass and reproduction are assumed to return to normal immediately after the effects of the spill have dissipated.

The relatively high mortality rates of fish larvae are included in the biological effects submodel, since a high number of the larvae killed at the time of the spill would have died regardless of the spill. Larvae and older age classes are not assumed to be inhabiting the same environment concurrently, and their losses are calculated separately.

For waterfowl and mammals, losses to hunting are calculated assuming constant natural and hunting mortality rates over time after the spill. For all wildlife, losses to viewing are calculated as the number not left alive in present and future years as the result of the spill, after constant natural mortality (and hunting mortality) is subtracted.

Lost catch (or lost number hunted) as the result of area closures to fishing or hunting is also calculated in the biological effects submodel for each species or species group. Catch lost due to closure, but no due to mortality, is added to mortality-induced catch loses to calculate total lost catch. Total lost catch by season, year and habitat type is output to the economic damages submodel where monetary damages are calculated.

The biological effects submodel was designed to be generally applicable, while restricting the data and parameter requirements to information which is readily available. Thus, biological data were compiled for a series of habitat types within each of the lakes in the Great Lakes region, as opposed to specific information for each possible geographic location.

Data contained in the biological data base are seasonal estimates of fish biomass per area (grams wet weight per square meter), numbers of birds and mammals per area, and rates of production for low trophic levels (plants and invertebrates).

Parameters required for the biological submodel include estimates of natural and fishing (hunting) mortality rates, available from the fisheries and wildlife literature; age-specific growth rates, available from length- or weight-at-age catch data; and age at recruitment and life span. The spawning areas and time for fish species, and development information for the young of all species groups are also required. All of these parameters are included in the data base as specific to habitat within each geographic region.

The economic damages submodel calculates damage to both commercial and recreational fisheries. The quantity of fish which would have been harvested in the absence of the incident is an output of the biological effects submodel. The value of the reduction in harvest or other use minus the cost of harvesting or using the resources is the lost in-situ use value of the resource. This provides a measure of the damages resulting from the spill.

Damages resulting from injury to lower trophic-level, non-commercial organisms are based on the ultimate loss in the in-situ use value of predator species (commercial and recreational fisheries, waterfowl and shorebirds, and mammals) which occurs when an incident affects the productivity of the food web. The food web model developed in the biological effects submodel quantifies the biological injuries which arise over time as a result of the incident. Economic damages are measured using the concepts and data applicable to commercial and recreational fisheries, to waterfowl and shorebirds, and to mammals.

Injury to waterfowl and shorebirds in losses of consumptive (hunting) and non-consumptive (e.g., viewing, photographing) in-situ use values. The quantification of biological injury to waterfowl and shorebirds is an output of the biological effects submodel. Damages resulting from losses in consumptive use are measured using available estimates of the marginal value of an additional waterfowl (duck or goose) harvest. Damages arising from losses in non-consumptive use value for non-game species are measured by employing an estimate of the marginal change in visitor days associated with a change in bird population for a wildlife refuge. Lost visitor days are evaluated in terms of monetary damages based on published unit day values.

Damages caused by injury to public beaches are measured as the lost use value of a length of beach, which depends on the season, the type of public beach affected and the extent and duration of the injury.

The system also includes a restoration component (French et al., 1991), which allows for situations in which restoration of injured resources may result in faster recovery of resources. Losses are computed with and without restoration, to determine which results in the shortest recovery time. This determination is made for each habitat type affected by the spill.

TRANSPORTABILITY

The entire model system has been programmed in a modular and generic fashion to facilitate applications to new areas. For computation of oil and chemical transport and fates, coastline and bathymetric data sets must be compiled. Transport currents can be computed and stored externally, or the hydrodynamic model embedded in the system can be initialized for the new study area. Information on shoreline types is recommended for oil spill modeling.

For assessment of biological impacts, the model requires information on the distribution of habitats, which may be inferred from bottom type, dominant vegetation type, and depth, plus wetland information along shorelines. Other necessary biological data are seasonal estimates of fish biomass per area (kg wet weight/km^2), numbers of birds and mammals per area (#/km^2), and rates of production for lower tropic levels (plants and invertebrates, g C/m^2/day). Parameters required for the biological submodel include estimates of natural and fishing (hunting) mortality rates, available from the fisheries and wildlife literature; age-specific growth rates, available from length- or weight-at-age catch data; age at recruitment (to the fishery); and life span. The spawning areas and times for fish species and development information for the young of all species groups are also required. All of these estimates are included in the data for each species in each geographic region.

Assessment of economic damages requires consumptive and non-consumptive values for all natural resources impacted by a spill. Consumptive values required are for

(1) commercial and recreational fishing (e.g. $/kg, by species)
(2) wildlife (e.g. $/individual hunted or trapped, by species)

Non-consumptive values needed are, for example:

(1) wildlife viewing (e.g. $/individual)
(2) beach use ($/m/day)
(3) recreational boating ($/km^2/day
(4) recreational useage of wetlands or other shoreline areas ($/km^2/day)

Non-use, or option and existence values may also be included. In general, these will be in terms of value per individual, and may apply to birds, mammals, endangered species, habitats, or broader geographic areas.

CONCLUSIONS

A comprehensive model for natural resource damage assessment has been presented. The model consists of three central submodels: physical fates, biological effects, and economic damages. These are supported by auxilliary submodels for hydrodynamic and restoration calculations, a GIS and associated data bases, and an extensive chemical data base. The entire system has been programmed in a modular and generic fashion, to facilitate transportability and applications to new areas, including marine and freshwater, tropical, temperate, and arctic environments.

Example applications have not been included here because the model has not yet been released for public review. However, a demonstration version of the software is available from the authors. The model system is near completion, and should be available for public review in the summer of 1991.

REFERENCES

Reed, M., D. French, S. Feng, and W. Knauss, 1990. A Three-Dimensional Oil and Chemical Spill Model and Coupled Geographical Information System. Proc. 1990 AMOP Conference.

French, D., S. Pavignano, and K. Jayko, 1991. Modelling Restoration of Habitats Impacted by Chemical Spills. Proc. 1991 AMOP Conference (this volume).

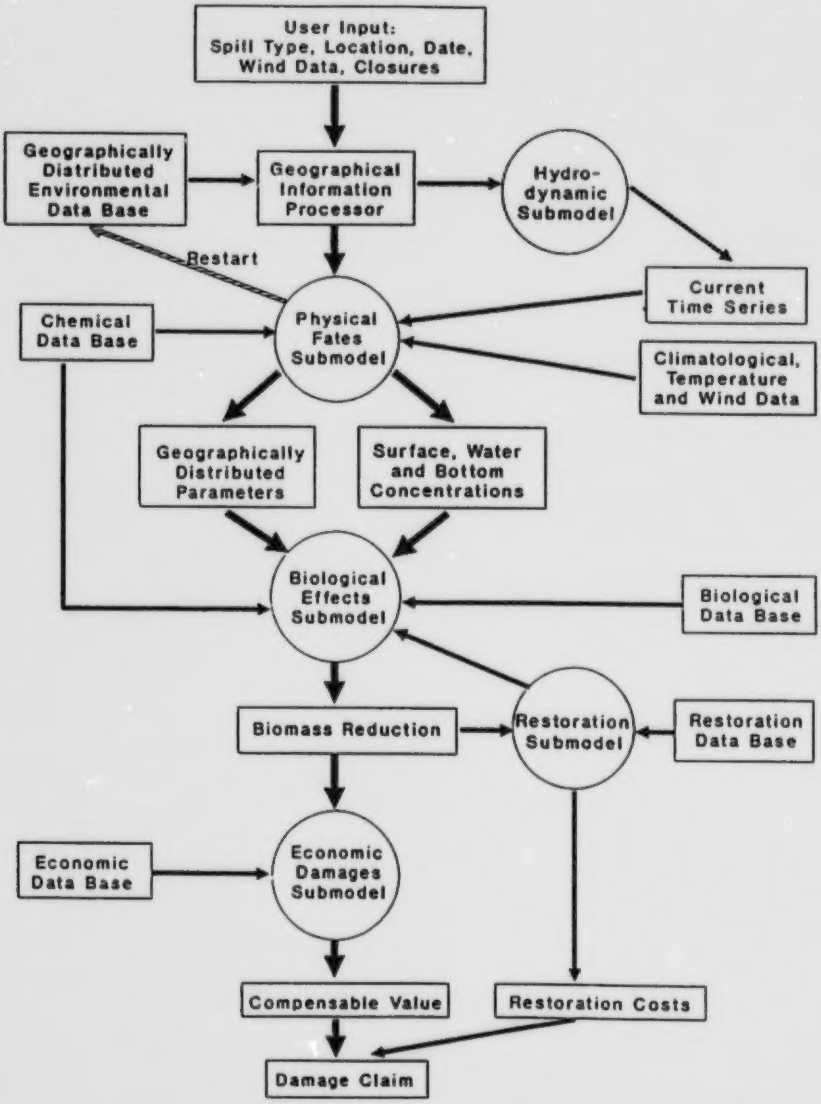
User Input:
Spill Type, Location, Date, Wind Data, Closures
Geographically Distributed Environmental Data Base
Geographical Information Processor
Hydro-dynamic Submodel
Restart
Current Time Series
Chemical Data Base
Physical Fates Submodel
Climatological, Temperature and Wind Data
Geographically Distributed Parameters
Surface, Water and Bottom Concentrations
Biological Effects Submodel
Biological Data Base
Biomass Reduction
Restoration Submodel
Restoration Data Base
Economic Data Base
Economic Damages Submodel
Compensable Value
Restoration Costs
Damage Claim

Figure 1 Schematic overview of the model system.

MODELLING RESTORATION OF HABITATS IMPACTED BY CHEMICAL SPILLS

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ABSTRACT

Estimation of natural resource damages resulting from spills of chemicals and oils is based both on the lost value of injured resources and on the costs for restoration or replacement of those resources. A model has been developed for use under the U.S. Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) which estimates injury resulting from spills and determines appropriate alternative actions for restoration which will reduce the injury. The model quantifies the net change in injury brought about by alternative actions and calculates damages from net injury and restoration costs.

INTRODUCTION

There is an ever increasing need for quantitative and objective assessments of environmental impacts (injury) and natural resource damages resulting from releases of toxic substances. Assessments are required for accidental spills, for chronic releases, for continuing contamination from historical dumping, for contaminants in discharges, for non-point sources, and for planning and management decision-making.

For assessments of large spills or significant loading, numerous field studies have been conducted in an attempt to measure injury. In a few cases, dollar valuations have been placed on these injuries to assess damages. However, these event-specific field efforts are expensive, time consuming, and difficult to coordinate because of the need for a number of researchers in several fields. Additionally, the results are often difficult to interpret or incapable of demonstrating injuries because of lack of enough baseline information before contamination occurred and the high degree of natural variability in both time and space which can obscure pollutant-induced changes.

Clearly there is a need for event-specific assessments of injuries and damages. However, the magnitude of the problem does not allow for detailed site-specific studies in every case. What is required is that studies be designed in a scientific manner, i.e., in such a way that hypotheses regarding cause and effect are developed and tested at particular sites so that the results may be extrapolated to other sites which may not have been studied in such detail. Furthermore, controlled laboratory studies can be of considerable use in developing hypotheses if it can be shown that the processes under study are not significantly altered by containment in a laboratory setting.

Numerical models are powerful tools in environmental impact and natural resource damage assessment. A model represents a hypothesis (or best-estimate of injury and damages) which is quantitatively stated and may be tested, modified and retested using laboratory and field observations. The consequences of a set of hypotheses may be explored using numerical models. Integrated numerical model systems may be used to quantify environmental impacts of real events or of hypothetical spill or management scenarios. These integrated model systems must include physical, chemical and biological components. If monetary damages are to be assessed, an economic component may be incorporated as well.

The desirability of compensating the public for damages resulting from spills of chemicals into the environment prompted passage by the United States federal government of the 1980 Comprehensive Environmental Response, Compensation, and Liability ACT (CERCLA). This act allows for compensation by a responsible party for costs associated with spill response, as well as resulting damages to natural resources.

In recognition of the fact that it is not reasonable or possible to perform an elaborate site-specific assessment for all spills, CERCLA provides for two types of damage assessment methodologies: type A, standard simplified procedures requiring minimal field observations, and type B, more complex and detailed studies for conducting assessments in situations which warrant further attention. The U.S. Department of the Interior (DOI) has developed procedures for type B assessments (Federal Register, August 1, 1986, 51 FR 27674) which involve considerable site- and event-specific effort. For type A assessments, a numerical model system was developed which allows a user to quantify damages with minimal effort and data input required. The first version of the type A model, the Natural Resource Damage Assessment Model for Coastal and Marine Environments (NRDAM/CME), was completed early in 1987 (Federal Register, March 20, 1987, 52 FR 9042; Economic Analysis, Inc. and Applied Science Associates, Inc., 1987; Reed et al., 1989; Reed, 1989;

French and French, 1989; Feng, Reed, and French, 1989; Grigalunas, Opaluch and Tyrrell, 1989; Grigalunas et al., 1989). The model has been further developed by Reed, French, and others to allow for greater spatial and temporal resolution and to be used with a Geographic Information System (GIS). This version will be used for Great Lakes applications as the Natural Resource Damage Assessment Model for Great Lakes Environments (NRDAM/GLE).

The type A models (NRDAM) contain three major components (Figure 1): the physical fates and biological effects submodels, which estimate the injury resulting from the spill, and the economic damages submodel, which values the injuries to assess damages. The injury determination and quantification is assessed for each of a series of habitats affected by the spill. Environmental, chemical, and biological databases supply required information to the model system for computation of fates and effects (injury). The user supplies information regarding the nature of the spill (time, place, chemical, and amount spilled) and some limited environmental conditions at the time (such as wind data).

Based on physical-chemical parameters such as density, solubility, vapor pressure and molecular weight, the physical fates submodel determines how much of the spilled material evaporates into the atmosphere, spreads as surface slick (oil and petroleum products), is dissolved in the water and settles to the bottom. A surface slick spreads and is transported by wind and currents, with continual evaporation into the atmosphere and entrainment and dissolution into the water column. Slicks interact with shorelines, depositing and releasing material according to shoreline type. Material in the water column is dispersed by mixing and is transported by currents. A portion of the dissolved substance may evaporate into the atmosphere or be adsorbed by suspended particulate matter. These particles sink to the bottom at a certain rate, and in this way dissolved substances will reach the sediments. A heavy substance will sink directly to the bottom with entrainment of water into the plume. Material reaching the seafloor is mixed into the sediments. Sedimented material may be resuspended and dissolved into the water column. Degradation and dispersive processes eventually reduce concentrations to below toxic thresholds for the exposed biota.

The physical fates model computes dissolved concentrations in the water column and the sediments, and the area and shoreline covered by a surface slicks in space and time. This information is passed to the biological effects submodel, which then calculates the biological effects of those concentrations.

The biological submodel utilizes habitat-specific and seasonally-varying estimates of the abundances of fish, shellfish, birds and mammals, and the productivity of plant and animal communities at the base of the food chain, in the environment of the spill to determine biological injuries. Deaths of fish and shellfish adults, juveniles and larvae are based on time of exposure of these organisms to toxic concentrations. Birds and mammals are affected only by surface slicks and shoreline oil.

Lost production of plants and animals at the base of the food chain is also computed. Lost production of fish, shellfish, birds and mammals due to this reduction in food supply is estimated using a simple food web model.

The biological effects submodel computes reduction of catch of fish and shellfish in the present and future years using standard fisheries models. Lost catch, includes losses due to mortality of adults, juveniles and larvae due to the spill. Using similar models, the numbers of birds and mammals missing and not hunted in present and future years are also calculated.

The economic damages submodel of the NRDAM/CME utilizes in situ use values for fisheries and wildlife hunting plus non-consumptive use values for wildlife (such as viewing) and beaches to calculate damages resulting from injury to natural resources. In the NRDAM/GLE, the damages also include recreational boating and non-use valuations (inclusive of existence, option, bequest values) of wildlife. These are damages due to lost or disrupted services of natural resources.

One of the major innovations in the NRDAM/GLE is the estimation of damages from the costs of restoration or replacement of natural resources and their services as well as damages based on the lost value of injured resources. Indeed, CERCLA calls for the use of restoration and replacement costs as the preferred measure of damages (43 CRF 11.35, see also Ohio v. DOI, 897 F.2d 1151, D.C. Cir. Court, 1989). Revised DOI procedures for natural resource damage assessments utilized in the NRDAM/GLE are summarized as follows:

(1) Quantify the injury to natural resources in terms of lost or disrupted services.

(2) Determine alternative actions which would restore (or replace) the resources and services in a cost-effective manner.

(3) Damages include lost services over the time required to accomplish the restoration, i.e., consideration is given to the ability of the resource to recover and the value of the lost services through the recovery period.

(4) As recognized by the U.S. Court of Appeals for the District of Columbia Circuit in its decision of July 14, 1989, restoration may not be "technically feasible" or the costs of restoration may be "grossly disproportionate" to the value of the lost services. In these cases, the value of the lost services is the appropriate measure of damages.

The following sections describe the methodology used to quantify injury to natural resources in terms of lost or disrupted services and the choices of alternative restoration and replacement actions assumed for the type A model. Consideration is given to the technical feasibility of actions and the ability of the resource to recover. A restoration action is considered technically feasible if it can be performed in such a way to reduce the injury to resources, and thus the damages. In order to reduce the injury, recovery following restoration actions must be faster than recovery with no action. If restoration is not technically feasible, actions which would replace the services otherwise provided by the natural resources are considered.

The biological effects submodel quantifies the injury to natural resources with and without the performance of alternative restoration and replacement actions. The alternative restoration and replacement actions are considered, habitat by habitat, for appropriateness based on the chemical spilled, conditions of the release, and natural recovery. The most technically feasible restoration response is chosen by the submodel. The economics submodel calculates damages associated with these injuries (using lost use and non-use values, termed compensable value). The costs of restoration or replacement are summed with compensable value resulting from injuries to natural resources to arrive at a final damages figure.

The following describes the concepts employed by the NRDAM/GLE. However, the concepts and methodology may be (and are) used to model other ecological systems than Great Lakes environments. The model is easily configured for any aquatic enviromental, including freshwater or saltwater, riverine, lake or pond, estuarine, marine and wetland habitats.

INJURY AND COMPENSABLE VALUE

The biological effects submodel estimates short-term losses resulting from a spill (i.e., losses at the time of the spill and while toxic concentrations remain in the environment) in terms of direct mortality and biomass not produced because of the loss of food resources. Losses are estimated by species or species group for fish and wildlife (birds and mammals).

The area potentially affected by the spill is represented by a rectangular grid of habitats with each grid cell coded as to habitat type. The habitat grid matches the sediment grid set up by the physical fates model using the GIS data base. A contiguous grouping of habitat grid cells with the same habitat code represents an ecosystem in the biological submodel. Fish, birds, mammals and rates of lower trophic level productivity are assumed constant and evenly distributed across an ecosystem within each of four seasons. Fish, birds and mammals are assumed to move at random within each ecosystem during a single season (whereupon they may move on). Fish eggs, larvae, and juveniles (i.e., young-of-the-year) are assumed constant and evenly distributed across each ecosystem within each month of an annual cycle. Planktonic stages are assumed to move with the currents.

Habitats include deepwater, nearshore, wetland and shoreline environments. Habitat types are defined by depth, proximity to shoreline(s), bottom type, dominant vegetation type, and the degree to which pollution stress presently exists.

A schematic of the biological effects submodel is shown in Figure 2. The physical fates submodel calculates surface slick locations and size, and dissolved concentration in three-dimensional space and in time. This information is passed into the biological effects submodel where the portion of exposed organisms in each habitat type which would be killed is calculated.

In the model, surface slicks (e.g., oil and petroleum products) interact with wildlife. A portion of those wildlife in the area swept by the slick are assumed to die based on probability of encounter with the slick and mortality once oiled. Estimates for these probabilities are derived from information on behavior and field observations of mortality under similar circumstances.

Fish and their eggs and larvae are affected by dissolved concentration (in the water or sediment). Mortality is calculated using laboratory acute toxicity test data (LC50, concentration lethal to 50% of test individuals) corrected for temperature and time of exposure, and assuming a log-normal relationship between percent mortality and dissolved concentration. For oil and petroleum products, LC50s for the most toxic component, the dissolved aromatics, are used. The movements of biota, either active or by current transport, are accounted for in determining time and concentration of exposure. Organisms killed are integrated over space and time and by habitat type to calculate a total short-term kill. This total short-term kill occurs from the time of the spill until the time the contaminant is dispersed to the point where dissolved concentrations are below toxic levels.

Biomass which is not produced as a result of a loss of food resources is estimated using a simple food web model. Lost primary (plant) and secondary (herbivore) production due to sublethal concentrations of spilled chemical is estimated using the LC50, the concentration where growth rate is 50% of the clean control, correcting it for temperature and assuming a log-normal relationship between percent of uninhibited growth rate and concentration. Primary and secondary production losses are integrated over space and time and by habitat to calculate the total weight not produced during the spill. For areas affected by sublethal concentrations, the rates of production are assumed to return to normal immediately following the dispersion of the spill to non-toxic concentrations.

For microalgae (phytoplankton and benthic microflora), concentrations which reduce production to near zero are essentially lethal. The above calculation procedure covers these losses. Reseeding of these groups into affected habitats which are no longer toxic is so rapid that recovery may be assumed immediate following dispersion of toxic concentrations. However, for macrophytes (aquatic plants and seaweeds), recovery following exposure to lethal concentrations is not immediate. In habitats dominated by macrophytes (e.g., wetlands), complete mortality of plants is assumed if a lethal threshold is reached (in water concentrations or in oil slick coverage). Losses from the direct kill and over the period of natural recovery after the toxicity is gone are included in the tabulation for macrophytes and for animals dependant on the wetland habitat (wildlife, fish, eggs and larvae and benthos).

The portion of the lost primary production which would have produced primary consumer (secondary producer or herbivore) biomass is estimated based on observations of ecological efficiency made on representative ecosystems. The fractions of the lost secondary production which would have been consumed by each of their predators (fish, birds and mammals) are assumed to be proportional to the biomass of that predator relative to the sum of its competitors. The output of this part of the submodel is lost production of the various fish, bird and mammal species or species categories as a result of the spill. This is added to the total direct kill to yield a total loss of biomass by habitat as a short-term result of the spill.

In addition to the direct kill and food-web losses (starvation) of eggs and larvae, fish young-of-the-year may be lost via habitat disruption. This is included in the submodel for wetland habitats destroyed by lethal concentrations or oiling. Losses are assumed proportional to the macrophyte loss. Thus, recovery of spawning and nursery habitat in wetlands follows recovery of macrophyte biomass and production.

Potential long-term losses (losses seen after the spill has dissipated) which can result from a spill of a toxic substance include: (1) lost recruitment to a fishery of the larvae and juveniles killed at the time of the spill; (2) lost future growth of the adults killed at the time of the spill; (3) changes in food web structure and, therefore, productivity of specific trophic levels and populations; and (4) chronic effects of sublethal levels of contaminants in tissues or the environment, such as reduced growth rate or loss of reproductive potential. The latter two effects are considered beyond the scope of this model, both due to the complexity of developing such models, which necessitates that they be both chemical- and site-specific, and to the lack of quantitative information required to run these models (e.g., see Hansen, 1984). Thus, the impacts estimated in the biological submodel are the results of acute toxicity and resulting direct effects on long-term productivity and yield: lost recruitment and lost growth. It is assumed that the spill has no indirect (chronic) effects or feedbacks after the spill has dissipated, such as changes in mortality due to density-dependent effects, changes in food web structure and predator-prey relationships, or changes in reproductive potential. The spill impact extends only for the life span of the species considered, and growth and reproduction are assumed to return to normal immediately after the effects of the spill have dissipated.

For fish, it is assumed that a constant natural mortality rate (due to natural causes) applies to juveniles over the age of one year and adults of a species; juveniles and adults inhabit the same habitat at the same time; there is a constant fishing mortality rate on adults; there is a constant survival rate over the first year of life; and the growth rate for adults past the age of recruitment to the fishery follows the von Bertalanffy relationship (Ricker, 1975). Using these assumptions and standard steady-state fisheries models, the age structure of a population and long-term losses in yield as the result of the spill may be estimated (Ricker, 1975). The initial kill in numbers by age is calculated from fish biomass killed, weight as a function of age, and natural and fishing mortality rates. For each year following the spill, the lost catch, calculated from fishing mortality, weight by age and average number alive during that year, is passed to the economic damages submodel. Thus, only those individuals which would have been caught in present and future years, and not those which would have died naturally, are included in the quantification of the effects of the incident.

The relatively high mortality rates of fish eggs and larvae are considered in the biological effects submodel, since a high number killed at the time of the spill would have died regardless of the spill. The young-of-the-year (eggs, larvae, and juveniles less than one year old) of each fish species category are tracked as percents of the age one population. Young-of-the-year and older age classes are not assumed to be inhabiting the same environment concurrently, and their losses are calculated separately.

For waterfowl and mammals, losses to hunting are calculated assuming constant natural and hunting mortality rates over time after the spill. For all wildlife, population losses are calculated as the number not left alive in present and future years as the result of the spill, after natural and hunting mortality is subtracted.

Lost catch (or lost number hunted) as the result of area closures to fishing or hunting is also calculated in the biological effects submodel for each species or species group. Catch lost due to closure, but not due to mortality, is added to mortality-induced catch losses to calculate total lost catch. Total lost catch by season, year and habitat type is output to the economic damages submodel where monetary damages are calculated.

The biological effects submodel was designed to be generally applicable, while restricting the data and parameter requirements to information which is readily available. Thus, biological data were compiled for a series of habitat types within each of the lakes in the Great Lakes region, as opposed to site-specific information for each possible geographic location.

Data contained in the biological data base are seasonal estimates of fish biomass per area (kg wet weight/km^2), numbers of birds and mammals per area (#/km^2), and rates of production for lower trophic levels (plants and invertebrates, g C/m^2/day). Parameters required for the biological submodel include estimates of natural and fishing (hunting) mortality rates, available from the fisheries and wildlife literature; age-specific growth rates, available from length- or weight-at-age catch data; age at recruitment (to the fishery); and life span. The spawning areas and times for fish species and development information for the young of all species groups are also required. All of these estimates are included in the data base for each species in each geographic region.

RESTORATION AND REPLACEMENT

The restoration and replacement model component of the biological effects submodel determines possible alternative restoration actions, whether those actions are technically feasible (i.e., whether those actions can be performed in such a way to reduce the injury), the cost effectiveness of the actions, and what alternative replacement actions for services lost might be performed if direct restoration is not feasible. This determination is made for each of the habitat types affected by the spill.

The basic assumptions of the model are as follows:

(1) Alternative restoration actions for each habitat type which have been documented (in the literature) as most effective in reducing injury and which represent the most cost-effective methodology for doing so are considered possible actions to be taken.

(2) A restoration action is assumed to be performed on a habitat over the area where it is technically feasible to reduce the injury.

(3) After restoration and recovery of the habitat are complete, restocking of fish and wildlife is assumed performed if stocks can be provided at the age the lost individuals would be at the time the habitat is recovered and can support restocked individuals.

(4) The reduction in injury brought about by restoration actions on habitats and restocking of fish and wildlife is subtracted from the injury calculated as resulting from the spill. The net injury represents services lost as the result of the spill. The value of these lost services is the compensable value portion of the total damages.

(5) Only restoration actions performed on the habitat affected are assumed to reduce the total injury and damages to the public. Actions such as buying up or protecting equivalent habitats do not restore what is lost because of the spill. Habitat enhancement or creation elsewhere cannot replace the lost individuals any faster than the assumed actions of restoration of the affected habitat and restocking, so at a minimum are equivalent in cost to the assumed actions. Restoring the affected habitat is most cost-effective.

(6) If restoration of habitats is not technically feasible, the chemical mass remaining in the environment at the time the spills effects have dissipated is assumed mitigated since it represents a loss of the services of natural resources to absorb pollutants (i.e., some of the assimilative capacity of the environment has been utilized, reducing the environment's ability to assimilate more pollutant mass).

(7) Mitigation of the remaining mass in Great Lakes habitats is assumed accomplished by removal of an equivalent toxic mass (as normalized by the LC50) from the environment. The mitigating chemicals are assumed to be removed by treatment of existing highly-contaminated sediments, since the ultimate fate of most chemicals is in the sediments.

Mitigating actions are assumed to be taken only where technically feasible, as defined above. Assumed actions for each habitat and medium are summarized below.

(1) Water column: No direct restoration possible, chemical mass remaining in water is mitigated by removal of an equivalent toxic mass in sediments.

(2) Atmosphere: Chemical mass entering the atmosphere is considered outside the scope of the model.

(3) Open water habitat sediments: contaminated sediment is dredged and refilled with clean material in shallow water areas (<30 feet) and in rivers. In deep waters, contaminated sediment is capped. Remediation by removal of contaminated sediment is the most common practice, as reviewed by USEPA (1982, 1988). Special dredging methods must be used to minimize the release of contaminants into the water column and these are assumed used in the model. Capping has proven feasible in depositional environments where future dredging and scouring will not occur (Lunz et al, 1978; Truitt et al, 1989). Thus, capping is assumed to be appropriate for quieter deep-water areas.

(4) Wetlands: Where warranted (i.e., where injury can be reduced), contaminated substrate is removed, replaced with clean equivalent, and replanted with a species distribution appropriate to the wetland type. This drastic action is only warrented where contamnation is lethal and natural recovery would be extemely slow because of long-lived residual contamination. In less extreme cases, only replanting is warrented. If contamination is non-lethal and short-lived, natural recovery is the alternative action resulting in the least damage, according to the model and recent literature on the subject (e.g., Cox and Cowell, 1979; Vandermeulen et al. 1981; Zieman et al., 1984; Getter el al, 1984; Baca et al., 1985, 1987; Michel, 1989; Brown, 1989; Ballou and Lewis, 1989).

(5) Shorelines: Shorelines are cleaned by washing (sand, gravel), replacement (mud) or steam cleaning (rock and artificial) where damages to public uses (such as beach use) warrant. It has been noted that experience from oil spills has shown that shoreline cleanup has done more harm ecologically than the original oil contamination, even for crude oil spills where oil remains on the shoreline for extended periods of time (Ganning et al, 1984; Cox and Cowell, 1979; Foster et al, 1990; NOAA as quoted by Golob's Oil Pollution Bulletin, 1990 regarding the Exxon Valdez case). Thus, shoreline cleaning would be called for to reduce damages due to public use or non-use valuation of shorelines, not for reduction of biological injuries. These assumptions are made in the model.

(6) Restocking of fish and wildlife is performed after recovery of the habitat if injury can be lessened by such action and if stocks at the appropriate ages are available.

An action is assumed to be performed on a habitat over the area where performance of that action would reduce the total injury as measured by compensable value (lost use and option and existence values). The injuries considered include those to biota and those to resources used or valued by the public. Thus, while reduction in sediment contamination in open water or wetland habitats reduces the injury to biota, the restoration actions on shorelines will most likely be warranted if they reduce losses of beach use.

To determine if injuries and resulting damages are lessened, it is assumed that restoration actions are started at the time it takes to mobilize for such actions following the spill. The area restored is that area where complete mortalities occur plus that area still toxic (i.e., over the threshold for effects) at the time both the restoration and following recovery are complete. For other areas, the recovery following restoration would not be complete until after natural recovery, and no net gain would result from direct action on the habitat. Figure 3 shows schematics which demonstrate where restoration actions will reduce injury.

Because of the nature of the alternative actions assumed in the model, it is assumed that the restoration action first completely destroys the habitat. Recovery is assumed to proceed over a time period indicated by field studies of newly-created clean habitat. The choice of action or no action is made by calculating the total injury and damages resulting in that habitat with and without the action performed as prescribed.

For natural recovery, the degree of recovery is measured by the difference between population sizes and production with and without toxic concentrations in the environment. Reproduction of fishery and wildlife species is assumed to resume normal levels as soon as toxicity to those life stages is no longer present. Immigration of new adults into the area is assumed to occur seasonally, whether the area remains toxic or not. Each spawning season, the number of eggs released is assumed to be as normal, but if the environment remains toxic, some of these are assumed killed.

If a wetland is affected by a complete kill (by oiling or lethal concentration), the recovery process of the macrophytes and animals directly dependent on the habitat (benthos and fish young-of-the-year) is assumed to follow a sigmoidal pattern. At first, recovery is slow because of time for reseeding of appropriate species and early succession. Later the recovery rate is much faster as indigenous species and the community grow to maturity. Finally, the last part of the recovery period proceeds slowly while organic matter builds up in the soil and benthic communities reestablish the ecological balance of a mature wetland. For offshore and nearshore habitats where restoration has been performed (capping or dredging and refilling), the recovery process is also assumed sigmoidal.

If restoration of a wetland is performed, it is assumed that the recovery process follows the same function as the natural recovery process after a complete kill. However, the timing is advanced due to the replanting which eliminates the reseeding lag.

For wetlands where there has been a complete kill, restoration (at least in the form of replanting) will always improve the situation by lessening the biological injury. If the kill of the wetland is incomplete (i.e., effects are sublethal for the macrophytes), there will rarely be a situation where restoration actions will lessen the injury. If, however, the toxicity is very long-lasting (in the sediments), the injury might be lessened by removal of substrate, refilling and replanting. The biological submodel calculates whether the injury is lessened as described above.

The total damages resulting from the spill include (1) the compensable value for the net loss of services of natural resources (including the effects of the restoration actions) and (2) the costs of accomplishing the restoration and replacement actions selected based on the assumptions outlined above. The actual restoration actions assumed to be taken, therefore, depend highly on the chemical and circumstances of the spill.

USE OF MODELLING FOR NATURAL RESOURCE DAMAGE ASSESSMENTS

The NRDAM/GLE and similar model systems may be used to quantify the physical fates, biological impacts and economic damages resulting from release of pollutants into aquatic environments for a wide variety of purposes. Natural resource damage assessments under CERCLA are just one example application. The relative impacts of various spill scenarios may be used to focus research efforts or legislate controls on potential polluters. Maximum liabilities for accidental spills may be estimated. The results of various management strategies may be investigated. A model system may be used to educate the public on the potential impacts of various spill scenarios.

The valid application of any model, including NRDAM/GLE, requires that none of the underlying assumptions of the model be significantly violated. In other words, if the "answer" based on the assumptions of the model is significantly different than the "real answer" because of some simplifying assumptions, use of the model may not be appropriate. However, the "real answer" is rarely, if ever, known. Therefore, an understanding of which assumptions are most influential to the answer is important to the user of the model.

The relative importance of the various assumed parameters in the model may be examined by sensitivity analysis, i.e., by varying the values assumed and determining how influential these changes are to the answer. However, on a more basic level, the main underlying assumptions of the model should be met for the "answer" to have a valid basis.

Integrated numerical model systems such as the NRDAM/GLE are a working set of hypotheses. Thus, they can and should be continually updated as new information becomes available. As such, they are extremely powerful tools in environmental impact and natural resource damage assessments.

REFERENCES

Baca, B.J., C.G. Getler and J. Lindstedt-Siva, 1985. Freshwater oil spill considerations: protection and cleanup. p. 385-390 In: Proceedings 1985 Oil Spill Conference, (Prevention, Behavior, Control, Cleanup), American Petroleum Institute, Environmental Protection Agency and U.S. Coast Guard, Feb. 25-28, 1985, Los Angeles, CA.

Baca, B.J., T.E. Lankford and E.R. Gundlach, 1987. Recovery of Brittany coastal marshes in the eight years following the Amoco Cadiz incident. p. 459-464 In: Proceedings 1987 Oil Spill Conference, (Prevention, Behavior, Control, Cleanup), American Petroleum Institute, Environmental Protection Agency and U.S. Coast Guard, Apr. 6-9, 1987, Baltimore, Md.

Ballou, T.G. and R.R. Lewis III, 1989. Environmental assessment and restoration recommendations for a mangrove forest affected by jet fuel. p. 407-412, In: 1989 Oil Spill Conference, (Prevention, Behavior, Control, Cleanup), American Petroleum Institute, Environmental Protection Agency and U.S. Coast Guard, Feb. 13-16, 1989, San Antonio, Texas.

Brown, J.D., 1989. Successful natural resource damage claim for a coastal oil spill. p. 293-296, In: 1989 Oil Spill Conference, (Prevention, Behavior, Control, Cleanup), American Petroleum Institute, Environmental Protection Agency and U.S. Coast Guard, Feb. 13-16, 1989, San Antonio, Texas.

Cox, G.V. and E.B. Cowell, 1979. Mitigating oil spill damage - ecologically responsible cleanup techniques. In. The Mitigation Symposium: A national workshop on mitigating losses of fish and wildlife habitats. U.S.D.A. Forest Service, Fort Collins, Colorado, p. 121-128.

Economic Analysis, Inc. (EAI) and Applied Science Associates, Inc. (ASA) 1987. Measuring Damages to Coastal and Marine Natural Resources: Concepts and Data Relevant for CERCLA Type A Damage Assessment, Vol. I and II. U.S. Department of the Interior, CERCLA 301 Project, Washington, D.C., January 1987.

Feng, S., Reed M., and French, D.P. 1989. The chemical data base for the natural resource damage assessment model system, Oil and Chemical Pollution, Vol. 5, 165-193.

Ganning, B., D.J. Reish and D. Straughan, 1984. Recovery and restoration of rocky shores, sandy beaches, tidal flats and shallow subtidal bottoms impact by oil spills. P. 7-36. In, J. Cairns, Jr. and A.L. Buikema, Jr. (eds.). Restoration of habitats impacted by oil spills, Butterworth Publishers, Boston, 182 p.

Getter, C.D., G. Cintron, B. Dicks, R.R. Lewis III, and E.D. Seneco, 1984. The recovery and restoration of salt marshes and mangroves following an oil spill. p. 65-113. In: J. Cairns, Jr. and A.L. Buikema, Jr. (eds.), Restoration of Habitats Impacted by Oil Spills, Butterworth Publishers, Boston, 182 p.

Golob's Oil Pollution Bulletin, 1990. NOAA finds no net environmental benefit from rock washing in Exxon Valdez cleanup. Golob's Oil Pollution Bulletin, World Information Systems, Vol. 11, No. 15, July 20, 1990, p. 7-8.

Grigalunas, T.A., Opulach, J.J., French, D.P. and Reed, M. 1989. Perspective on validating the natural resource damage assessment model system, Oil and Chemical Pollution, Vol. 5, 195-215.

Grigalunas, T.A., Opulach, J.J. and Tyrrell, J.J. 1989. The Economic Damages Component of hte Natural Resource Damage Assessment Model System, Oil and Chemical Pollution, Vol. 5, 195-215.

Hansen, D.J., 1984. Utility of toxicity tests to measure effects of substances on marine organisms. p. 33-56. In: H.H. White (ed.), Concepts in Marine Pollution Measurements, Maryland Sea Grant Publ., Univ. of Maryland, 743 p.

Lunz, J.D., R.J. Diaz and R.A. Cole, 1978. Upland and wetland habitat development with dredged material: Ecological considerations. Technical Report DS-78-15. U.S. Army Waterways Experiment Station, CE, Vicksburg, Miss., 50 p.

Michel, J., 1989. Natural resource damage assessment of the *Amazon Venture* oil spill. p. 303-306, In: 1989 Oil Spill Conference, (Prevention, Behavior, Control, Cleanup), American Petroleum Institute, Environmental Protection Agency and U.S. Coast Guard, Feb. 13-16, 1989, San Antonio, Texas.

Reed, M., 1989. The physical fates component of the CERCLA type a model system, Oil and Chemical Pollution, Vol 5, 99-123.

Reed, M., French, D.P., Grigalunas, T. and Opaluch, J., 1989. Overview of a natural resource damage assessment model system for coastal and marine environments. Oil and Chemical Pollution. Vol. 5, 85-97.

Ricker, W.E., 1975. Computation and interpretation of biological statistics of fish populations. Bull. Fish. Res. Board Can. VOl. 191, 382. p.

Truitt, C.L., J.E. Clausner and T.N. McLallan, 1989. Considerations for capping subaqeous, dredged material deposits. J. Waterway, Port, Coastal, Ocean Eng., 115(6):741-759.

U.S. Environmental Protection Agency (USEPA), 1982. Handbook: Remedial action at waste disposal sites. Municipal Environmental Research Laboratory, Office of Environmental Engineering and Technology, Office of Research and Development, U. S. Environmental Protection Agency, EPA-625/6-82-006. NTIS PB 82-239054, March, 1982.

U.S. Environmental Protection Agency (USEPA), 1988. Guidance for conducting remedial investigations and feasibility studies under CERCLA. Interim Final, Office of Emergency and Remedial Response, U.S. Environmental Protection Agency, Washington, DC, EPA/540/G-89/004, October 1988.

Vandermeulen, J.H., B.F.N. Long and L. D'Ozouville, 1981. Geomorphological alteration of a heavily oiled saltmarsh (Ile Grande, France) as a result of massive cleanup. p. 347-351, In: Proceedings, 1981 Oil Spill Conference, (Prevention, Behavior, Control, Cleanup), American Petroleum Institute, Environmental Protection Agency and U.S. Coast Guard, March 2-5, 1981, Atlanta, Georgia.

Zieman, J.C., R. Orth, R.C. Phillips, G. Thayer and A. Thorhaug, 1984. The effects of oil on seagrass ecosystems. p. 37-64. In: J. Cairns, Jr. and A.L. Buikema, Jr. (eds.), Restoration of Habitats Impacted by Oil Spills. Butterworth Publishers, Boston, 182 p.

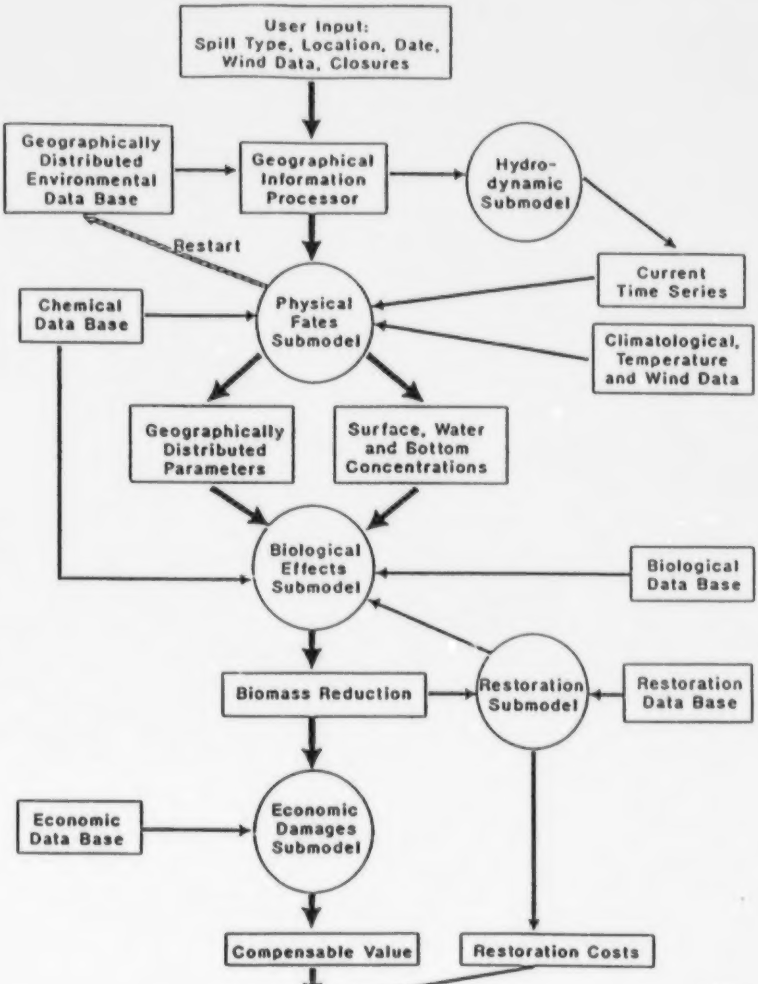
User Input:
Spill Type, Location, Date,
Wind Data, Closures
Geographically Distributed Environmental Data Base
Geographical Information Processor
Hydro-dynamic Submodel
Restart
Current Time Series
Chemical Data Base
Physical Fates Submodel
Climatological, Temperature and Wind Data
Geographically Distributed Parameters
Surface, Water and Bottom Concentrations
Biological Effects Submodel
Biological Data Base
Biomass Reduction
Restoration Submodel
Restoration Data Base
Economic Data Base
Economic Damages Submodel
Compensable Value
Restoration Costs
Damage Claim

Figure 1 Schematic overview of the model system.

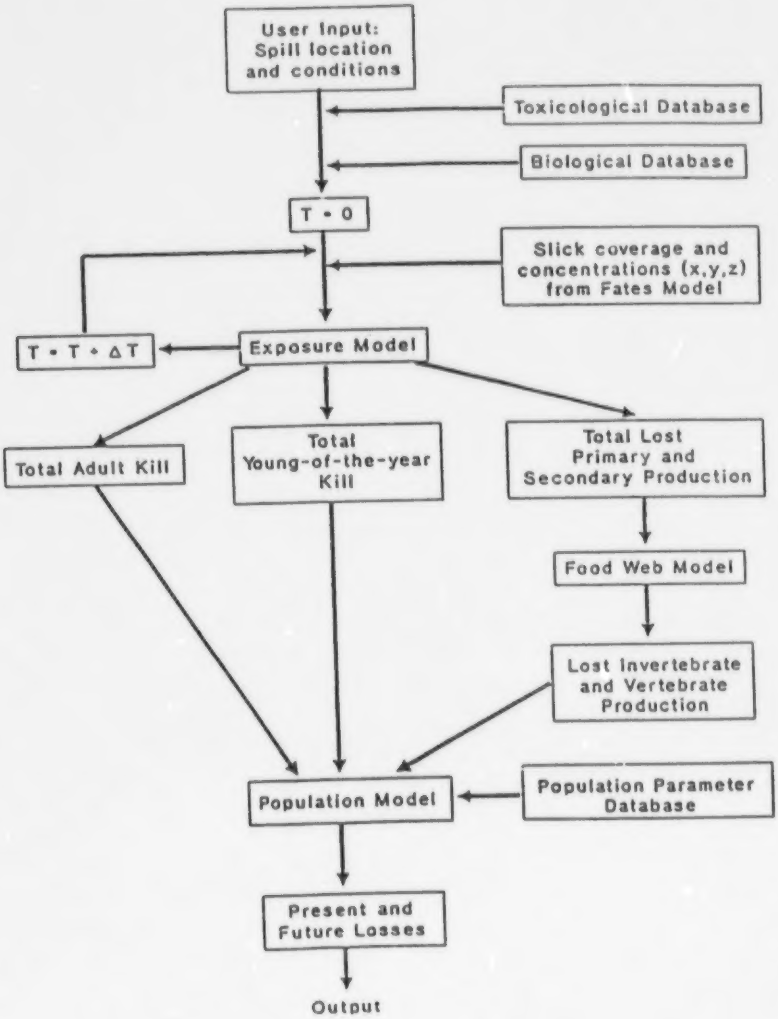
User Input:
Spill location
and conditions
Toxicological Database
Biological Database
T = 0
Slick coverage and
concentrations (x,y,z)
from Fates Model
T = T + ΔT
Exposure Model
Total Adult Kill
Total
Young-of-the-year
Kill
Total Lost
Primary and
Secondary Production
Food Web Model
Lost Invertebrate
and Vertebrate
Production
Population Model
Population Parameter
Database
Present and
Future Losses
Output

Figure 2. Schematic of the biological effects submodel for calculation of injuries.

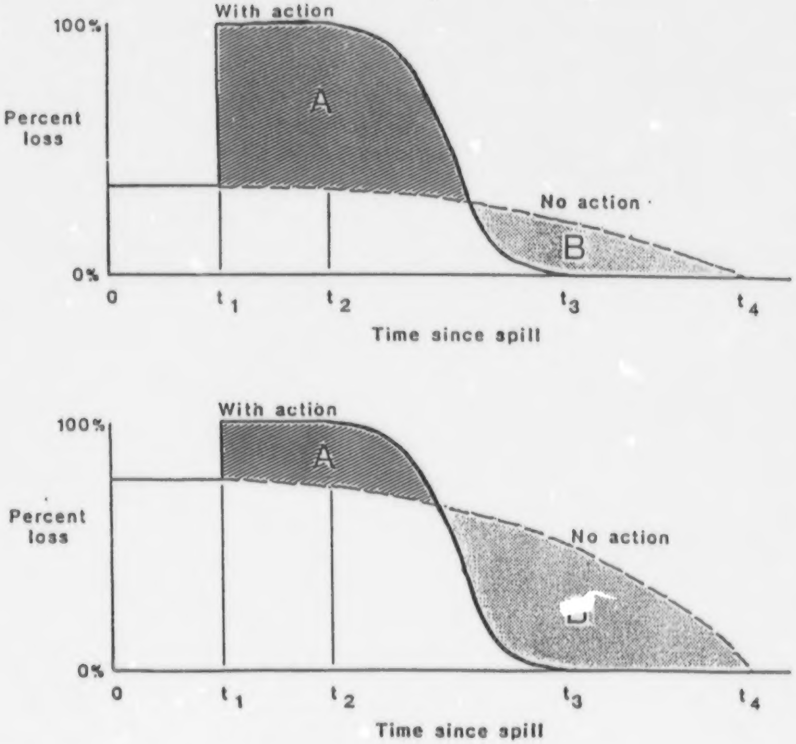

Figure 3 Schematics showing cases where restoration will not reduce the injury (upper graph, area A > area B) and where restoration will reduce the injury (lower graph, area A < B). The times of events are: t_1 = time work on site begins, t_2 = time work on site is completed, t_3 = time recovery is complete assuming restoration action performed, t_4 = time habitat is no longer toxic assuming no restoration action is performed (i.e., assuming natural recovery).

The Application of a Chemical Model for the Assesment of Risk.

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Introduction

In 1978 the World Health Organization (WHO) defined risk as the expected frequency of the occurence of an undesirable effect arising from exposure to a chemical or physical agent [1]. This definition can be summarized by equation 1 ;

$$\text{RISK} = \sum \text{HAZARDS} \times \sum \text{EXPOSURES}$$

Equation 1

where risk has units of % change from normal populations. Hazard is defined as the likelihood that an injury will occur at a given exposure, has units of % change per dose, and is usually measured as a non-linear response. Exposure is a quantitative term measured directly from a specific environmental situation with units of dose.

This equation can be applied to calculate the increased risk which a population will experience as a result of a given exposure to a substance of known hazard. More importantly, by rearranging this equation as in equation 2, the exposure that produces a given risk can be calculated for a known hazard[2].

$$\Sigma \text{ EXPOSURE} = \frac{\text{TOTAL RISK}}{(\Sigma\text{HAZARDS})}$$

Equation 2

That is to say if a risk of 1 in 10^6 is agreed as socially acceptable and the hazard is immediate death at a known exposure level, then we can calculate the exposure that corresponds with this acceptable risk. This exposure could occur in a single, acute dose or could be built up from repeated or continous doses over time. If the exposure is then averaged over a period of time, values similar to the well established IDLH and TLV values can be determined. Furthermore, if the same concepts are applied to chemical spills, the tolerable levels associated with a spill of a specific substance can be defined. Knowing the rates of accidents per unit distance traveled then the risk of transporting this chemical can be determined. Given a constant acceptable risk, the priorities in security of transport can be established directly from the hazard values of materials.

For the last ten years, our laboratory has been developing a chemical model for the experimental determination of hazard. This report will discuss our progress, along with a review of some of the relevent risk and exposure concepts, so that a more comprehensive explanation of the relationship of the basic science to TLV, IDLH, can be established as well as, the development of a hazard based spill priority list.

Preliminary Concepts

The components of the WHO risk equation have been traditionally examined as separate issues. This section will briefly present some of the aspects of these issues.

Risk

The concept of risk is a very difficult parameter convey to the general population in a comprehensible way. This difficulty arises as a result of the statistical nature of this parameter, as well as, the inadequate language of risk. The most common way to express risk is as a statistical increase in the incidence of disease or death relative to a control population. For example, an increased risk of 1 in 10^6 is routinely chosen as the limit of acceptable risk[3]. This value is based on what can be significantly measured above the control. Even so it is difficult to convey the meaning of this value in a real since. Often a relative value is used to convert this value into laymans terms, unfortunitaly this often acts to undermine the danger of the risk ie) odds of 1 in 10^6 have been related to the odds of being hit by lightning and killed, or the risk associated with eating one peanut butter sandwitch every day for 70 years[3].

The selection of an acceptable risk translates to making a judgement of the value of life realtive to the achievement of other goals. In North America, political debate has evolved from an initial "zero acceptable risk" position to the present value of 1 in a million. The significance of this value is still a topic of much debate[3]. It has been suggested that the level of exposure after a spill event should be returned to the level of background[4]. This appears like a very reasonable objective, however, it must be realized that this background should be site specific. In the last century many industrial chemicals and by products have been released into the environment. The consideration of these compounds as background leads to an increased acceptable risk for the populations incontact with these chemicals. If chemical spills are only cleaned up to a level that reflects this higher acceptable risk, then over time, the background levels will undoutedly increase, effectively lowering life expectancy and increasing disease levels.

Hazard

The hazard that a chemical will induce is traditionally inferred from a statistical series of animal studies followed by an in depth histological analysis of the sacrificed dosed animals relative to a control group of animals. Significant deviations from the control group are attributed to the chemical being tested. The quality and suitability of these data are major limiting factors in determination and understanding the hazard. In the limit of this work, if the variance of the hazard data is high, then even if acceptable total risk is agreed, acceptable exposures cannot be defined.

In all cell types, intrusion of a xenobiotic chemical leads to some type of damage at the molecular level. This ability to cause injury may also be defined as the toxicity of the chemical. For this reason, assays based on the nature and extent of primary damage hold the best potential for predicting disease. Unfortunately they also hold the most potentail for a number false positive or negitive indications. This initial intoxication may be ameliorated by protecive responses but it is an essential precondition for disease. Because of these protective capabilities, the net hazard can be factored into two major types of responses.

$$\text{Hazard} = \{(\text{toxicity by chemical}) - (\text{protection by host})\} / \text{dose}$$

Equation 3

The protective responses of an individual are designed as either short or long term reaction to a perturbation in cellular equilibrium. They are limited by the cellular resources and overall health of the individual and are thus finite. Signs of disease occur when the primary damage or toxic response overwhelms the protective response in situations of short term overdose or stress due to long term exposure.

Short term biochemical assays measure the toxic response by inhibition kinetics or by metabolite analysis. In contrast some short term tests such as the Ames assay and most long term studies of chronic exposure to a toxin define the total hazard in terms of tissue pathology or whole body disease. An ideal assay would be to combine these capabilities. This can be achieved if the biochemical test identifies the amount of initial chemical derangement which is known to lead inevitably to disease end points. These end points may be short or long term so that one test would surfice for both acute and chronic hazard assessment. This experimental system could also be used to study the effect of environmental parameters such as stress and nutrition on the overall effect of the chemical.

Our laboratory has been evaluating the rat hepatic microsomal Mixed Function Oxidase (MFO) system as a possible system for defining the environmental hazard of xenobiotics[5-8]. The active component, Cytochrome P-450, is an enzyme capable of metabolizing essentially all organic chemical groups. The role of the so called, phase I enzyme is to hydroxylate exogenous and endogenous lipophilic chemicals, thereby lowering their lipophilicity for the purpose of transport within, or excretion from, the organism by phase II systems. Usually this enzyme functions as intended, achieving detoxification by elimination. However, for a significant number of xenobiotics, some alternately oxidized metabolites of this system become more toxic than the parent chemical. If these metabolites become suicidal[9], the MFO system can participate in both the initiation and promotion of cancer and is therefore an ideal model to establish a short term assay of primary damage, which is intimately coupled to the long term hazard of the disease.

The development of a short term indication of the toxicity of a chemical or class of chemicals depends in turn on the validation of the Quantitative Structural Activity Relationships (QSAR) which exist between the structure of the xenobiotic molecule and the hazardous responses on reactivity which they induce. Once the QSAR is available it can lead to the development of a computer based modeling program that could predict hazards of existing or new chemicals without animal testing. This would not only provide a humane and publicly acceptable option to animal testing, but also provide a practical tool to evaluate the over 10,000,000 organic chemicals known.

Exposure Monitoring

Traditionally, exposure measurements or model calculations are only concerned with defining the concentration of a xenobiotic that reaches the outermost protective layer of the person or animal (biosystem) of concern. More specifically, these layers are the outermost surface of the skin, digestive system, and lung. However, the ultimate necessary of hazard value is defined at the cellular level, therefore, it is important to be able to calculate the relationship between a concentration of a xenobiotic at this barrier and the concentration at the site of action, the cell.

At the present time the most commonly used parameter to predict the intercellular availability is the octanol/water partition coefficient. This value gives a rough indication of the lipophilicity of the xenobiotic, and thus its affinity for the barrier wall relative to the protective moisture that is associated with most of these walls. However, it is obvious that the transport through epithelium tissues is a much more complex process than the partitioning between octanol and water. Dermal transport studies using ^{14}C labeled compounds have been performed on Sprague-Dawley rats and Rhesus monkeys in an attempt to produce a more accurate indication of transport rates[10,11] and mechanisms. In addition numerous pharmacokinetic studies have been performed to determine the fate and spread of selected drugs and pollutants throughout the body.

The next difficulty involved in exposure calculations is accounting for human variations in behavior. This parameter has a direct effect on human intake and thus exposure. It has been a general practice to overestimate the exposure contact an individual has in order to provide a `worst case scenario'[12]. However, it is important to choose consistant values reflecting the same relative population percentile, so that the calculated values can then be correlated to the average individual. Ideally, using the average exposure with an understanding of the relative variance and thus standard deviation would indicate the range of risk expected in the exposed population. An indication of some of the typical parameters considered for exposure calculations is presented in table 1 below.

Table 1[12]
Estimates and frequently cited ranges of parameters used in exposure assessment.

Parameter	Best estimate	Range of values
Uptake (air) adult	12 m3/day	10 to 25 m3/day
Ingestion (tap water) adult	1.2 L/day	.8-2.5 L/day
Ingestion (soil and dirt) toddler	25-40mg/day	25-10,000 mg/day
Ingestion (soil and dust) adult	5-10 mg/day	10-500 mg/day
Airborn dust area with dirt roads	200µg/m3	50-20000µg/m3
Ingestion(freshwater fish)midwesterner	10 g/day	6-300 g/day
Ingestion (tomatoes) American	30 g/day	10-200 g/day

There are commercial computer programs that are available (Aid for Evaluating the Redevelopment of Industrial Sites {AERIS}) or are being developed (Hazard Assessment of Chemicals in Soil {HESP}) that both estimate expected exposure and indicate the hazard resulting from this exposure. However the toxicological basis for the hazard assessment in these programs is limited. The utility of these programs has been discussed recently[13].

Applications of WHO Concepts

Acceptable Exposures

As examined in the previous discussion if a hazard is known and the dose-effect relationship well established, and if an appropriate acceptable risk is selected, then it is possible to determine the exposure that reflects this risk, or rather an acceptable exposure. An exposure value based on a real determined risk, is a much more valuable parameter for spill responders than the typical TLV commonly consulted. It has been suggested that the established exposure guidelines, such as the Threshold Limit Value (TLV), are not entirely based on such a scientific system. A statement by D.E. Hathway on the determination of TLV values illustrates the importance of perception factors in setting these values ;

> " ... unlike physical constraints, such values have no real scientific value, and are often based on limited evidence. At best, they represent an informed opinion

> about safe conditions, but they have no statutory significance. It is not surprising that these values get changed from time to time; usually in the downward direction. What is confusing is that TLV's are incommensurate with the risk involved. Thus, in 1981, benzene has a TLV of 10 ppm (in 1975, 25 ppm) and phenol of 5 ppm (in 1975, 5 ppm), but benzene presents a greater risk than phenol. It is fairly difficult to maintain an atmospheric concentration below the TLV in the case of benzene, but this does not apply to the less volatile phenol." [11] (underline added)

The underlined section of this quotation emphasises that elements beyond acceptable risk can be considered in the determination of TLV values. The relationship between `acceptable risk' and `acceptable exposure' is defined by the WHO equation even if it is not consulted. Therefore, the selection of a higher acceptable exposure limit for whatever reason translates instantly into permitting a higher acceptable risk for the population being exposed. Often a risk benefit analysis is considered before regulatory values are set. This analysis simply means that a higher level of adverse health effects is acceptable if the overall benefit to society `justifies' this cost. Unfortunitly the population being exposed does not often participate in the evaluation of this risk benefit analysis and in many cases the benefit is realized by a sub-population outside of the exposed population.

Spill Priority List

The spill priority list developed by Fingas et al[15], represents an implicit but indirect application of the WHO risk equation. However, the assessment of hazard based only on LD_{50} values of rats and fish limits its application to assessing the risk of immediate loss of life during the event. With an increased recognition of the long term risks associated with an accute event, as well as, the chronic exposure to the contamination remaining after redemial action, new risk models can be developed.

Conclusion

Our population is becoming more educated and sensitized to environmental issues, as this happens the demands placed on regulatory personel will increase expontially. The development of scientifically based regulatory values and priority systems is necessary so that we begin to reverse the degredation of our fragile environment.

References

1. World Health Organization. Principals and Methods for Evaluating the Toxicity of Chemicals Part I. Environ. Health Criteria, 6:19 (1978)

2. Brownlee, L.J. Chemical Control of the Mixed Function Oxidase System and its Implications in Determining Biological Hazard. Thesis Master of Science in Chemistry. Carleton University, 1990.

3. Royal Society of Canada. A Symposium on the Assessment and Perception of Risk and Human Health in Canada. edited by Bates, D.V,. & Rogers, J.T. Ottawa, 1983. ISBN 0-920064-18-3.

4. Greaney, D.L., & Hope, W.B. Emergency Response Risk Assessment and Environmental Contamination Cleanup Criteria. 4th Conference on Toxic Substances. Proceedings. p 173-184. Ministry of Supply and Services Canada. Ottawa, 1990 Cat. No. En 40-11/4-1990F

5. Boersma, D.C., Brownlee, L.J., & Hollebone, B.R., A Total Induction Index of Metabolism for Lipophilic Xenobiotics. J. Appl. Toxicol. 4:187-193 (1982)

6. Brownlee, L.J., & Hollebone, B.R., A Correlation of Induced Mixed Function Oxidase Specific Activity to C-H bond Strengths in Partially Chlorinated Monocyclic Hydrocarbons. J. Appl. Toxicol. 6:61-66 (1986)

7. Hollebone, B.R., Categorization of Lipophilic Xenobiotics by the Enthalpic Structure-Function response of Hepatic Mixed Function Oxidase. Drug Metab. Rev. 17:93-143 (1986).

8. Brownlee, L.J., Evans, C.H, & Hollebone, B.R., The Relative Induction of Mixed-Function Oxidase Specific Activity to C-H and C-Cl Bond Strengths in Polychlorinated Derivatives of Dibenzo-p-dioxin (PCDDS). J. Appl. Toxicol. 6:67-71 (1986).

9. Ortiz de Montellano, P.R., Mico, B.A., and Yost, G.Y. Suicidal Inactivation of Cytochrome P-450, Formation of a Heme-Substrate Covalent Adduct. Biochem. Biophys. Res. Comm. 83:132-4 (1978).

10. Moody, R.P., Benoit, F.M., Riedel, D., and Ritter, L. Dermal Absorption of the Insect repellent DEET (N,N-Diethyl-m-Toluamide) in Rats and Monkeys : Effect of Anatomical site and Multiple Exposure. J. Tox. & Envir. Health, 26:137-147, 1989.

11. Moody, R.P., and Ritter, L. Dermal Absorption of the Insectidide Lindane (1δ, 2δ, 3δ, 4δ, 5δ, 6β - Hexachlorocyclohexane) in Rats and Rhesus Monkeys : Effect of Anatomical site. J. Tox. & Envir. Health, 28:161-169, 1989.

12. Paustenbach, D.J., Important Recent Advances in the Practice of Health Risk Assessment : Implications for the 1990's. 4th Conference on Toxic Substances. Proceedings. p 121-168. Ministry of Supply and Services Canada. Ottawa, 1990 Cat. No. En 40-11/4-1990F

13. Kelly, K.E. International Approaches to Establishing Site Cleanup Levels : An Evaluation of Different Methods. 4th Conference on Toxic Substances. Proceedings. p 113-125. Ministry of Supply and Services Canada. Ottawa, 1990 Cat. No. En 40-11/4-1990F

14. Hathway, D.E., Molecular Aspects of Toxicology. The Royal Society of Chemistry. London, 1984.

15. Fingas, M.F., Stone, N., Leblanc, D., Sergy, G., Mansfield, B.H., et al. Development of a New Chemical Spill Priority List. p. 115-190. Proceedings of the Seventh Technical Seminar on Chemical Spills. Ministry of Supply and Services Cat. No. En 40-327/ 1990.

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EUROSPILL: CHEMICAL SPILL MODEL BASED ON MODELLING TURBULENT MIXING AT SEA

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ABSTRACT

This paper will describe how a 3-dimensional advection-diffusion equation is solved using the results of sea trials spanning 5 years. Particular attention will be given to the processes of evaporation and solution where the critical parameters are the surface area of the slick and the mass transfer coefficients for evaporation and solution. A user-friendly random walk particle-tracking model is used to follow the motion of individual parcels of chemical to reproduce the observed spreading of chemicals on the surface of the sea and in the water column. In addition, experiments at sea in 1990 using slicks of sparingly soluble and volatile chemicals have provided new data which enables estimation of the mass transfer coefficients for solution and evaporation. These results obtained at sea will be compared with values obtained by theory, laboratory work, and work with dissolved gases at sea.

1. INTRODUCTION

Warren Spring Laboratory (WSL) in conjunction with the Unit for Coastal and Estuarine Studies (UCES) and the Stazione Oceanographica (Italy) has developed a user-friendly computer model (Eurospill) for oil and chemical spills at sea. Eurospill has a modular structure which is controlled by a menu-driven user interface. The user interface enables data to be entered or retrieved from the model and acts as a controlling program for the numerical models which are used to determine the fate of a spill. This approach means that the user does not have to be aware of methods of data entry to the separate models and the interaction between them. Hence, the model is simple to operate, although the science behind it is complex, and is intended to provide rapid predictions for use in response to real spills, risk analysis, contingency planning and training.

Eurospill predicts the behaviour of oils and chemicals at sea on the basis of their physical properties and the turbulent mixing of the sea. The main processes which determine the fate of a chemical at sea are: spreading, dispersion, reaction, evaporation, and solution. Of these processes, spreading and dispersion are dominated by the action of the sea (Murray, 1972; Elliott, 1986; Elliott *et al.*, 1986), whilst reaction, evaporation and solution are more dependent on physical properties (although clearly the turbulent mixing plays a critical role by determining the surface area of the slick via the spreading term).

The major route for the disappearance of the surface chemical slick at sea, for many chemicals, is via the processes of evaporation and solution. This paper will outline the first documented attempts to derive, in a systematic fashion, the rate of evaporation and solution of chemicals from experimental releases at sea.

2. EQUATIONS FOR THE RATE OF EVAPORATION AND SOLUTION

The rate of solution and evaporation for a chemical spilt at sea can be described by the generalised equations:

$$\frac{dM_S}{dt} = k_S S A \tag{1}$$

$$\frac{dM_E}{dt} = \frac{k_E M P A}{RT} \tag{2}$$

Thus, the mass transfer rate (dM/dt) is dependent on physical properties of the chemical (such as its solubility, S; vapour pressure, P; and relative molecular mass, M), the surface area of the slick (A), and the mass transfer coefficients for evaporation and solution.

The physical properties of the chemical can be obtained from data tables and various data bases.

A corner-stone for Eurospill is the way in which it models the spreading of slicks in terms of oceanic processes, rather than treating slicks at sea as an extension of chemicals or oils spreading on the surface of a pool of water in a laboratory test tank. Eurospill produces a realistic prediction of the size, shape, and non-uniformity of the slick. The modelling of the spreading and hence the surface area of the slick will be described briefly here and in more detail in a talk entitled " Spreading of Oil Slicks by the Action of Turbulent Mixing at Sea" at the AMOP conference.

The mass transfer coefficient, or transfer velocity, is in effect a measure of the way in which environmental conditions, such as wind speed, modify the rate of evaporation and solution. This paper will concentrate on attempts to produce estimates of the mass transfer coefficients for the processes of evaporation and solution at sea, from field data collected at sea.

3. THE SURFACE AREA TERM

The way that Eurospill models the spreading of slicks is based on work carried out in conjunction with UCES. The modelling of spreading is only discussed briefly here as there are several references in the literature which cover the area in greater depth (Elliott, 1986; Elliott *et al.*, 1986; Elliott & Wallace, 1989; and Elliott & Hurford, 1989).

The basis of the approach is that the slick spreads due to the turbulent mixing in the surface layers of the sea rather than the process being dominated by the physical properties of the chemical such as viscosity and surface tension (as in the Fay approach -Fay, 1971). A random walk particle-tracking model is used to solve the generalised 3-dimensional advection-diffusion equation:

$$\frac{\partial C}{\partial t}+\frac{u\partial C}{\partial x}+\frac{v\partial C}{\partial y}+\frac{w\partial C}{\partial z} = \frac{\partial}{\partial x}(K_h\frac{\partial C}{\partial x})+\frac{\partial}{\partial y}(K_h\frac{\partial C}{\partial y})+\frac{\partial}{\partial z}(K_v\frac{\partial C}{\partial z})+\delta_s-\delta_r \quad (3)$$

∂C/∂t is the accumulation of chemical at a point in the water column. The u, v and w terms describe the advection of the chemical and have three independently acting components due to tide, wind, and waves. Those involving K_h and K_v are diffusive terms and describe the random exchange of fluid parcels in the turbulent mixing of the sea. δ_s and δ_r are source and removal terms which describe the processes of solution and evaporation respectively.

In Eurospill, the advection-diffusion equation is solved by modelling the slick as a distribution of particles. Each particle, which can be thought of as equivalent to droplets of chemical, is advected and dispersed by the near surface currents. Evidence that an oil patch can be considered as individual droplets which will be transported by currents and turbulence within the water column has been provided by Forrester (1971) who observed oil droplets beneath a slick at depths exceeding 20m.

There are vertical gradients in the surface currents due to tide, wind, and waves, with the highest velocities nearer the surface. Thus, the degree to which each droplet is advected is dependent on the amount of time it spends in the surface layers relative to the deeper waters. This in turn is determined by the balance between the buoyancy and the vertical diffusion rates. Thus, larger more buoyant droplets spend proportionately more time in the surface layers and are advected further due to the surface currents. The spreading of the slick is therefore controlled by the droplet size distribution and shear diffusion processes. The model correctly predicts the occurrence of thicker chemical or oil towards the leading edge of the slick and the alignment and elongation of the slicks in the direction of the wind. This is in marked contrast to the uniform circular or elliptical slicks predicted by variations on the Fay approach (*eg*. Fay, 1971; Lehr *et al*., 1984). Another important improvement on the Fay-type approach is that the effects of tide, wind, and waves are parameterised. So, accurate predictions can be obtained for rough seas where it is difficult to obtain empirical data.

As stated in the conclusions of a recent review of oil spill modelling (Spaulding, 1988) when discussing spreading via shear diffusion, "This advance explains many important observed features of oil spill spreading and will likely replace the Fay algorithm in future model development modifications". At present Eurospill is one of the few chemical and oil spill models which follows the spreading of the slick by considering the action of the turbulent mixing of surface waters.

4. MASS TRANSFER COEFFICIENTS FOR EVAPORATION AND SOLUTION

In addition to the term for the surface area of the slick in equations 1 and 2, the other important terms to determine are the mass transfer rates for evaporation and solution (k_g and k_s).

There are few data available for mass transfer coefficients determined at sea, but laboratory derived coefficients are available from the literature. The work that is published in the literature can be split into two categories: those where the processes of evaporation and solution are looked at independently by the study of floating chemicals; and those where information is obtained both for k_g and k_s from the study of the evaporation of soluble gases and chemicals from the water column.

An example of the first type of experiment using floating chemicals comes from Mackay and Matsugu (1973) who formulated the empirical relationship:

$$k_g = 0.029\ U^{0.78}\ X^{-0.11}\ Sc_G^{-0.67} \tag{4}$$

based on laboratory work which directly measured the rate of evaporation from a floating pool of chemical. U is the wind speed at a height of 10m, X is the pool diameter, and Sc_G is the gas phase Schmidt number [viscosity / (density x diffusivity)].

The second group of experiments obtain estimates of k_g and k_s from work on dissolved gases (Liss and Slater, 1974; Liss and Merlivat, 1986) and dissolved organics (Mackay and Leinonen, 1975; Mackay and Yeun, 1983). The basis for this is the two resistance model for fluxes across the air-sea interface described by Liss and Slater (1974). This states that for a dissolved gas to pass into the atmosphere across the air-sea interface it has to overcome two resistances (the resistance being the reciprocal of the mass transfer coefficient): one from the water it is dissolved in ($1/k_s$) and one from the air above the interface ($1/k_g$). The two resistances contribute to the overall mass transfer coefficient according to the formula:

$$\frac{1}{k_{Overall}} = \frac{1}{k_s} + \frac{RT}{Hk_g} \tag{5}$$

where H, the Henry's Law Constant, is the vapour pressure divided by the solubility. Thus, once the overall mass transfer coefficient has been calculated, by studying the rate of evaporation of a dissolved gas or chemical, it is possible to obtain information on both k_g and k_s.

For relatively low solubility compounds where H is large (*eg*. CO_2, CH_4, O_2, and N_2) the liquid phase resistance, k_s, is dominant. Thus, work on dissolved gases has produced an estimate of the dependence of k_s on wind speed, U, (Liss & Merlivat, 1986):

$k_s = 0.17U$ for $U \le 3.6$ ms^{-1}
$k_s = 2.85U - 9.65$ for $3.6 < U \le 13$ ms^{-1}
$k_s = 5.9U - 49.3$ for $U > 13$ ms^{-1}

These relationships have been confirmed by laboratory and field measurements of dissolved gases (Liss and Merlivat, 1986), and in particular there have been some experiments with gaseous tracers in the North Sea which have confirmed that the relationship seems to hold even at wind speeds 17.5 ms^{-1} (Watson *et al*., 1991). However, it is not possible to apply the mass transfer coefficients for dissolved gases directly to those for dissolved organics - for example the molecular diffusivisities of the two classes of compounds differ. The way in which Watson *et al*. (1991) relate k_s for two different gases is to use the a power law relationship with the liquid phase Schmidt number Sc_L:

$$(k_S^1/k_S^2) = (Sc_L^2/Sc_L^1)^{0.51}$$

If this correlation is applied to CO_2 ($Sc_L = 600$) and BDGA ($Sc_L = 1860$) then the values derived by Liss and Merlivat (1986) for CO_2 need to be divided by a factor of 1.78.

The equations which WSL used in advance of this work were those from the work of Mackay and Yeun (1983) on the rate of evaporation of dissolved organics:

$$k_g = 1x10^{-3} + 46.2x10^{-3}\ U^*\ Sc_G^{-0.67}$$

$$k_s = 1x10^{-6} + 34.1x10^{-4}\ U^*\ Sc_L^{-0.5} \qquad \text{for } U < 5ms^{-1}$$

$$k_s = 1x10^{-6} + 144x10^{-4}\ U^{*2.2}\ Sc_L^{-0.5} \qquad \text{for } U > 5ms^{-1}$$

Where the friction velocity, $U^* = (6.1 + 0.63U)^{0.5}\ Ux10^{-2}$

However, these estimates of mass transfer coefficients are based on work in the laboratory rather than releases at sea. Clearly the lack of validation with sea trials is a serious source of concern. Thus, the Marine Pollution Control Unit (MPCU) of the Department of Transport funded a series of sea trials aimed at obtaining data which can be used to obtain estimates of the mass transfer coefficients for evaporation and solution at sea.

4.1 EXPERIMENTAL METHODS

The form of the chemical releases at sea is to pump chemicals from a 200 litre drum at a fixed rate of 2 litres per minute from a moored dinghy (in water depth of 40m). The chemical which is pumped out onto the sea surface is taken downstream by the tidal currents so that when chemical is released for several hours at a fixed rate, from a fixed source, a steady state plume of chemical is produced. The distance from the discharge dinghy can be related to time in the water as the speed of the tidal current can be measured. These continuous releases allow increased repeatability because data can be collected many times at the same diffusion time. Time resolution is also improved, to around 10-20 seconds (which represents a resolution of 10-20m in distance along the length of the plume). Because of these clear benefits in experimental design, we would hope that other workers in this field will also start to use steady state plumes for some experiments, rather than releases of single patches of chemical which are difficult to follow and even more difficult to sample effectively without disturbing the slick.

The chemicals used for the sea trials were a mixture of acetates with a variety of vapour pressures and solubilities. In this way it is possible to correlate the rates of evaporation and solution with the physical properties of the chemical and thus ensure that the results from these sea trials can be extrapolated to releases of any chemical.

A method of pad sampling was developed for floating chemicals. The person sampling leans forward from the bows of a small inflatable boat and places an absorbent pad 30x30 cm onto the surface of the undisturbed slick. To aid the location of the slick the acetates were mixed with dye (around 100g of "oil red o" per 200L of acetates).

The absorption of the acetate onto the pad will clearly not be quantitative since the pad will not absorb all the chemical from a given area. Therefore, the mixture of acetates released not only contains those used to follow the processes of evaporation and solution, but also an inert acetate (nonyl acetate) which is used as the reference against which the concentrations of the other acetates are measured. As the concentrations of all the acetates are measured against nonyl acetate this also accounts for the reduction in amount of chemical per unit area of slick which results from the slick dispersing and spreading over the surface of the water (i.e. both the reactive and inert acetates are "diluted" to the same extent as a result of the slick dispersing and spreading). Thus, the measured concentrations of the reactive acetates normalised to the inert one decrease with time due solely to the processes of evaporation and/or solution. This is an important feature of the experimental design.

A number of replicate samples at fixed distances from the discharge dinghy were taken during the sampling procedure. Once the sample was taken, the pad was placed in "Nalgene" plastic jars containing 150ml of hexane. This rendered the acetate mixture inert by extracting it into the hexane phase. On return to WSL the concentrations of acetates relative to nonyl acetate were measured by gas chromatography.

4.2 RESULTS

It is important at this stage of the discussion to stress that the data presented here are still at the initial stages of being processed. In particular, only the data from two of the acetates (Methyl Amyl Acetate [MAA] and Butyl DiGlycol Acetate [BDGA]) out of the four are presented here.

The information that can be gained from an acetate release is a plot of relative concentrations *versus* time. Figure 1 shows an example of rate of loss of the acetates by solution (Fig. 1a) and evaporation (Fig 1b). The rate of loss is exponential as predicted by the integration of the generalised equations for evaporation and solution. For example for solution:

$$-\frac{dM_s}{dt} = k_s SA \qquad (6)$$

Since A = M / hρ Where h = Thickness of the slick
ρ = Density of the chemical

$$-\frac{dM_s}{dt} = \frac{k_s S}{h\rho} M \qquad (7)$$

Integrate with respect to time:

$$\ln \frac{M_t}{M_o} = -\frac{k_s S}{h\rho} t \qquad (8)$$

$$M_t = M_o e^{-\frac{k_s S}{h\rho} t} \qquad (9)$$

As the rate of loss of the chemical is exponential (Equation 9), a plot of ln (M_t/M_o) *versus* time should produce a straight line of gradient $-k_sS/h\rho$ (Equation 8). Figure 2 shows that this is indeed the case for two of the 4 acetates released during the trial. From each of these straight line relationships it is possible to derive a value for the mass transfer coefficient for solution (BDGA, Butyl Diglycol Acetate) or evaporation (MAA, Methyl Amyl Acetate). In total there were 7 successful releases of chemical over a variety of wind speeds (from 3.0 to 11.5 ms^{-1}). The mass transfer coefficients calculated in these trials for the seven releases are compared to previous values quoted in the literature in figure 3.

4.3 DISCUSSION

Comparison of the mass transfer coefficient for evaporation (Fig. 3a) determined from the sea trials with Mackay and Matsugu (1973) shows that the latter overestimates the rate of mass transfer by a factor of around about 5. Comparison with the Mackay and Yeun (1983) relationship, however, shows a very close correlation. Thus the relationship, calculated on the basis of the two phase resistance model and laboratory experiments with dissolved organics, appears to be in good agreement with the experimental data collected at sea.

In the case of the mass transfer coefficient for solution it is possible to compare the values derived from these experimental releases with those predicted by Liss and Merlivat (1986) which have recently been backed up by experimental work with tracer gases in the North Sea (Watson *et al.*, 1991). The plot in figure 3b shows the Liss and Merlivat (1986) relationship corrected according a power-law dependence on the liquid phase Schmidt number (Watson *et al.*, 1991) - see section 4. The corrected Liss and Merlivat relationship falls very close to that derived by Mackay and Yeun (1983). Comparison with the data collected at sea by WSL shows that, while there is good agreement with literature values at lower wind speeds, above a wind speed of 5ms^{-1} the rate of mass transfer is overestimated. In particular, the mass transfer coefficient for solution does not increase to the same extent with increasing wind speed as predicted by the literature. This could be due to the well documented phenomenon of dampening of surface waves by the action of the surface slick, or it could be some other effect which can not be recreated by laboratory experiments. This clearly requires further investigation.

These findings have important implications not only for the rate of solution of a floating soluble chemical but also for the rate of evaporation of lower solubility organic compounds (which includes many of the chemicals which are carried in bulk at sea) from the water column. As mentioned in the discussion of the two phase resistance model, for low solubility compounds, where the Henry's law constant is large, the rate of evaporation from the water is determined by the water phase resistance (*ie*. the mass transfer coefficient for solution).

Work in the next few months with the other two acetates used in the sea trials (Methyl Cyclohexyl Acetate [MCA] and Butyl Glycol Acetate [BGA]) should provide further information on the mass transfer coefficients and, if appropriate, help to formulate new algorithms for the variation of k_s and k_g with wind speed.

5. CONCLUSIONS

Evaporation and solution are two important pathways for the dissipation of chemicals at sea. The two critical areas in the accurate determination of the rates of evaporation and solution are the surface area of the slick and the mass transfer coefficients for evaporation and solution.

One of the great strengths of Eurospill is that it models the way that a slick spreads on the surface of the sea in a realistic manner by modelling the turbulent mixing processes at sea. In addition, the fact that Eurospill models the spreading of the slick by the action of near surface current shears due to tide, wind and waves means that each of these environmental properties can be parameterised. Thus the model can produce accurate predictions of the rate of spreading for rough seas where it is difficult to obtain empirical data.

The sea trials carried out by WSL in 1990 represent the first attempt to determine the mass transfer rates for evaporation and solution using releases of chemicals at sea. The trials indicate that the relationship formulated by Mackay and Yeun (1983) for the mass transfer rate for evaporation agrees closely with the field data. However, first indications seem to show that the relationships for mass transfer for solution (Mackay and Yeun, 1983; Liss and Merlivat, 1986) over-estimate the mass transfer rate at wind speeds above $5ms^{-1}$. This has important implications for calculating the rate of solution of floating slicks and the rate of evaporation of chemicals dissolved in the water column - reducing the rates of both processes. So, while mass transfer rates for a floater-evaporator appear to be in good agreement with the relationship predicted by Mackay and Yeun (1983), it appears that, for dissolvers or dissolver/evaporators, the literature overestimates the mass transfer rates for their dissipation.

In conclusion, these new developments on the effect of oceanic forces on a slick and the results of trials at sea are incorporated into an extremely user-friendly PC-based computer model. So, not only is Eurospill "state of the art" in terms of scientific content but it also easy to use as a response tool or for contingency planning.

ACKNOWLEDGEMENT

The work on chemical releases at sea, including the preparation of this paper, is funded by the Marine Pollution Control Unit of the Department of Transport. I would also like to thank the Warren Spring staff that were involved in the collection of the sea trial data, often in difficult conditions.

REFERENCES

Elliott, A.J. Shear diffusion and the spread of oil in the surface layers of the North Sea. Dt. Hydrogr. Z. 39, 113-137, 1986.

Elliott, A.J., Hurford N. & Penn C.J. Shear diffusion and the spreading of oil slicks. Mar. Pol. Bull. 17, 308-13, 1986.

Elliott, A.J. and Wallace, D.C. Dispersion of surface plumes in the southern North Sea. Dt. Hydrogr. Z. 42, 1-16, 1989.

Elliott, A.J. & Hurford N. The influence of wind and wave shear on the spreading of a plume at sea. Oil & Chem. Pol. 5, 347-363, 1989.

Fay, J.A. Physical processes in the spread of oil on a water surface. Proceedings of the Joint Conf. on the prevention and control of oil spills, 15-17 June, Publ. by API, 463-7, 1971.

Forrester, W.D. Distribution of suspended oil particles following the grounding of the oil tanker Arrow. J. Mar. Res. 29, 151-170.

Lehr, W.J. A new technique to estimate initial spill size using a modified Fay-type spreading formula. Mar Pol. Bull. 9, 326-329, 1984.

Liss P.S. & Slater P.G. Flux of gases across the air-sea interface. Nature 247, 181-184, 1974.

Liss P.S. & Merlivat L. Air-sea gas exchange rates: Introduction and synthesis. In The role of air-sea exchange in geochemical cycling Ed. Buat-Menard, P. 113-127 Publ. Reidel Dordrecht, 1986.

Mackay D. & Leinonen, P.J. Rate of evaporation of low-solubility contaminants from water bodies to the atmosphere. Environ. Sci. Technol. 9, 1178-80, 1975.

Mackay D., & Yeun A.T.K. Mass transfer correlations for volatilisation of organic solutes from water. Environ. Sci. Technol. 17, 211-17, 1983.

Mackay D., & Matsugu R.S. Evaporation rates of liquid hydrocarbon spills on land and water. Can. J. Chem. Eng. 53, 434-39, 1973.

Murray S.P. Turbulent diffusion of oil in the ocean. Limnol. Oceanol. 17, 651-660, 1972.

Spaulding, M.L. A state-of the-art review of oil spill trajectory and fate modelling. Oil Chem. Pol. 4, 39-55, 1988.

Watson A.W., Upstill-Goddard R.C., & Liss P.S. Air-sea gas exchange in rough and stormy seas measured by a dual tracer technique. Nature Vol. 349, 145-147, 1991.

Fig.1 MAA and BDGA concentrations relative to an inert acetate.
Concentrations decrease exponentially with time.

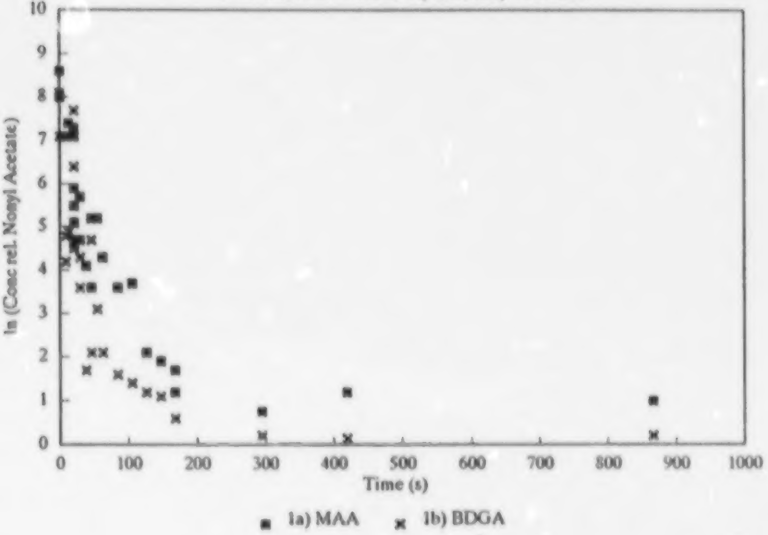
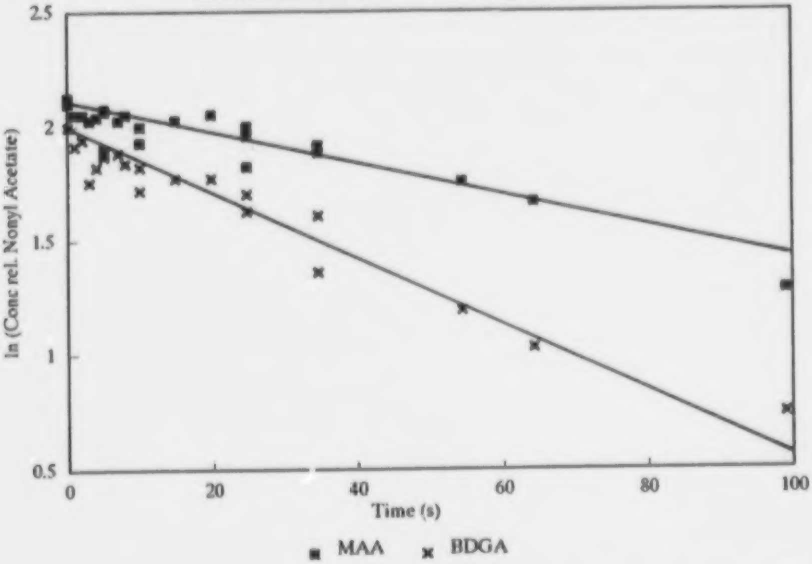


Fig.2 Natural log of MAA and BDGA concentrations vs time
Ks and Ke can be determined from the gradient of the plot



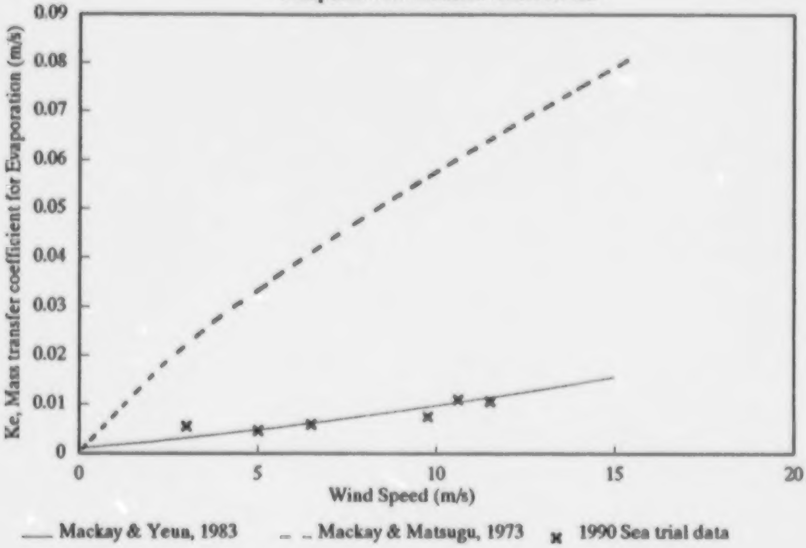


Fig.3 CHEMICAL TRIALS AT SEA 1990

Compared with literature values for Ke

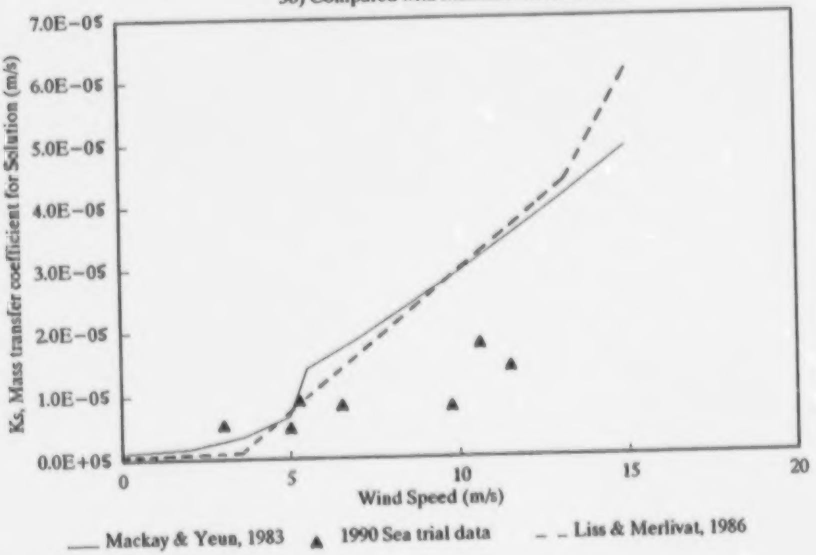


Fig.3 CHEMICAL TRIALS AT SEA 1990

3b) Compared with literature values for Ks

CRITICAL FRACTURE LENGTH IN A FIRE HEATED PRESSURE-LIQUEFIED GAS TANK

by

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Abstract

The present paper describes a model that estimates the critical fracture length of a fire heated pressure liquefied gas (PLG) tank. Cracks of certain sizes may result in a catastrophic failure of the container, possibly leading to a Boiling Liquid Expanding Vapour Explosion (BLEVE), or simply the release of contents through the opening. The model is applied to both cylindrical and spherical tanks and the results are compared with some available accident and experimental tank failure data.

Introduction

Pressure liquefied fuels have been widely accepted for domestic, commercial and industrial use since their introduction in the early twentieth century. Considerable quantities are stored and transported annually. The primary modes of transportation are road, rail and ship.

A number of recent accidents involving storage tanks and transport vehicles have produced extensive property damage, serious personal injury and many deaths. Major evacuations have also been necessary in some cases.

In 1979, a train derailment in Mississauga required the evacuation of almost a quarter of a million people for five days. The accident involved 24 rail tank cars, 2 of them containing LPG. A total of 3 of the tanks failed during the fire, luckily without human injury [1]. The 1984 accident at an LPG storage facility in Mexico City had tragic consequences. Five hundred people died and 7000 were seriously injured when most of the 6 spherical and 48 cylindrical LPG tanks failed catastrophically during a fire. More than 200,000 people [2] were subsequently evacuated to prevent further injury. The (American) National Fire Protection Association (NFPA) has documented 18 accidents involving LPG tanks that resulted in explosions prior to 1973 [3].

In a typical storage or transport fire incident the pressure-liquefied gas tank car is engulfed by a pool or impacted by a jet fire. The tank pressure rises rapidly as the contents are heated, resulting in rapid tank failure if the tank is not vented using suitably-sized pressure relief devices (PRD). Even if the tanks are vented, heat transfer from the fire to the tank wall and into the vapour space results in very high wall temperatures which can eventually result in tank failure.

Vapour wall failure can result in two possible outcomes: arrested development of the crack followed by discharge of the contents or rapid tank disintegration. If there is a major release caused by loss of containment, flash evaporation, if flammable, can lead to fire balls and/or explosions. The explosions can often be severe, with large pieces of the vessel being propelled more than a kilometer from their initial location [2]. This type of catastrophe is termed a **Boiling Liquid Expanding Vapour Explosion (BLEVE)**. The flying debris and contents may cause secondary fires between their origin and final destination. Vapour cloud explosions also result from this event [4].

The exact sequence of events leading to a BLEVE is not well understood. Reid [5] has suggested that a BLEVE is related to the behaviour of the hot liquid as the tank is very rapidly depressurized after containment failure.

In this paper we will present a hypothesis in the form of a simple model for containment failure. This model will be used to identify whether the tank rupture leads to a catastrophic flashing release, or whether the tank contents could be released *safely* through the *fracture formed*.

Fracture Initiation - What We Know

Our present understanding of the sequence of events that occur when a PLG tank is engulfed in fire is as follows:

1. The engulfing fire (or flare) causes the tank wall temperature to rise; heat transfer to the liquid and vapour components is initially by free convection.

2. This convection leads to significant stable vertical temperature stratification in both the liquid and vapour.

3. The low flow velocities that result from convection of the vapour cause the rate of heat transfer from the vapour space wall to reduce with time [6].

4. The liquid space wall heat flux causes boundary layers to form on the walls (except at the very bottom of the tank). These turn horizontally at the liquid/vapour interface, forming a thermally-stratified layer at the liquid surface. The surface temperature of this layer determines vapour pressure and thus the pressure within the tank. The temperature of this layer increases with time and, consequently, the tank pressure increases [6].

5. When the container pressure reaches the opening set point, the PRD opens. Material is discharged and the pressure is now influenced by both the lading heat transfer and material ejection through the device. Depending on the level of liquid the valve discharge may be single-phase, superheated vapour or a two phase fluid [6,7,8].

6. As material continues to exit, the liquid interface level drops and the exposed vapour space walls rapidly increase in temperature due to the poor heat transfer [6,9,10].

7. The rise in vapour wall temperature, and the associated reduction in tank material strength eventually leads to creep rupture of the hottest portion of the metal. Invariably, this occurs at a location dictated by the view factors of the engulfing pool fire, from the PRD discharge flare [11, 12] or the impact of jet fire.

Fracture Propagation - The Hypothesis

An energy balance model is developed to estimate the fracture length formed in the fire heated PLG vessel. Fracture formation, after initial creep, rupture is in its simplest form equated to the work potential of the vapour: i.e. the decrease in the internal energy of the system (the vapour) less the enthalpy of the fluid that has left the sytem.

In a cylindrical pressure vessel, the initial crack tends to propagate along the axis of the cylinder surface as shown in Figure 1. The crack then propagates radially along the wall. The crack is either, arrested at the centre of the tank, where the flange opening for the pressure relief device (PRD) is welded to the tank, or it continues to propagate circumferentially resulting in an end tub. This portion of the container can then be projected for considerable distances [2,13].

Baum [14] describes experiments on the axial rupture of unheated gas-pressurized 102 mm diameter mild steel pipes. His specimens were machined to provide an axial defect to initiate a crack. The pipes were then pressurized with air until the defect failed. Baum found that as the crack develops, the pipe wall undergoes lateral deformation adjacent to the free edges formed by the crack. His study of the breach formed indicates that only the

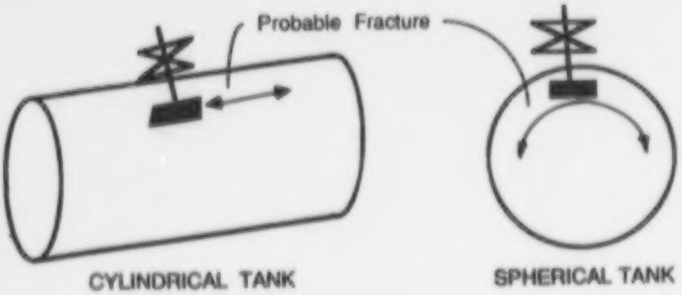

Figure 1: Fracture Propagation on a PLG Tank.

pipe wall within a circumferential distance equal to the tank radius, on either side of the defect is in motion. He noted that there was no arrest of the crack since the velocity of crack propagation was approximately matched by the speed of sound in gas. For superheated vapours, and propane in particular, the speed of sound is 200-250 m/s [15]; it is thus possible that the energy of the depressurizing wave could be exhausted prior to the crack reaching *cold* metal.

The crack propagation and steel deformation properties obtained in Baum's experiments [14] should therefore be quite similar to the crack propagation of a PLG tank except that the metal is now heated at least where the crack propagates in the vapour space. Metal temperatures are typically in the range of 450-500^{0}C [6,9,10].

The simple model that we propose for crack or fracture length analysis assumes that the energy for crack propagation comes from the vapour space pressure energy. The length of the crack formed can be estimated from the available energy of the vapour. It further assumes that the fracture propagation at the crack tip is ductile and that a circumferential distance R on either side of the crack deforms plastically. The hypothesis developed is as follows:

1. The length of fracture is proportional to the available energy in the vapour. The quantity of vapour space energy is that available from isentropic expansion of the vapour prior to rupture.

2. The vapour depressurizes through the initially ruptured location releasing its stored energy. This energy causes the crack to propagate into the vapour wall. The wall area at the tip of the fracture deforms plastically, with the fracture tip propagating in a ductile manner. At high temperature the flow stress is low, and the stress concentration around accumulated dislocations can be relieved by local plastic deformation and there is no transition to brittle fracture [16].

3. Transition to brittle fracture is possible if the wall temperatures are reduced [16].

4. To be consistent with Baum's [14] experimental findings, it is assumed that the region of the tank wall within a circumferential distance R (0.5 D) either side of the moving fracture deforms plastically. The tank wall within this region thin out evenly until its cross-sectional area reaches a minimum cross-sectional area, A_f, sufficient for tank integrity at the prevailing vapour wall temperature and tank pressure.

5. The maximum fracture length formed, therefore, can be evaluated by equating the total vapour space energy, and the energy require to plastically deform the tank wall to fracture length of I.

Theory

1) Available Vapour Space Energy

For the Isentropic Expansion of a perfect gas,

$$-W = M_1C_vT_1 - M_2C_vT_2 - (M_1-M_2)\,C_pT_2 \qquad (1)$$

$$T_2/T_1 = (P_2/P_1)^{\gamma-1/\gamma} \qquad (2).$$

However,

$$M_1 = (P_1 V / R_m T_1) , \qquad (3)$$

$$M_2 = (P_2 V / R_m T_2) , \qquad (4)$$

and $$C_p - C_v = R_m \qquad (5)$$

where $\gamma = C_p/C_v$ and

$R_m =$ Universal Gas Constant/Molecular Weight.

Substituting equations (2), (3), (4) and (5) in (1) and simplifying yields:

$$-W = V P_2/\gamma\text{-}1 \, [(P_1/P_2) - 1 - \gamma (P_1/P_2)^{1/\gamma} + \gamma].$$

Using the compressibility factor, Z, to correct for deviations from ideality yields for a non ideal gas:

$$-W = Z V (P_2/\gamma\text{-}1) [(P_1/P_2) - 1 - \gamma(P_1/P_2)^{1/\gamma} + \gamma]$$

2) Energy for Plastic Deformation for a Unit Length (Figure 2).

E_f = Force × Distance

Force = $\sigma_f (t \times 1)$

Distance = $2 R \times \epsilon_f$

$2 R (A_0 / A_f - 1)$

$\therefore E_f = 2 \sigma_f \, t \, R (A_0 / A_f - 1).$

where A_f/A_0 is the reduction in the wall cross section area and σ_f , the ultimate tensile strength at the vapour wall temperature.

The estimated fracture length is therefore,

$$l \quad = \quad -W / E_f$$

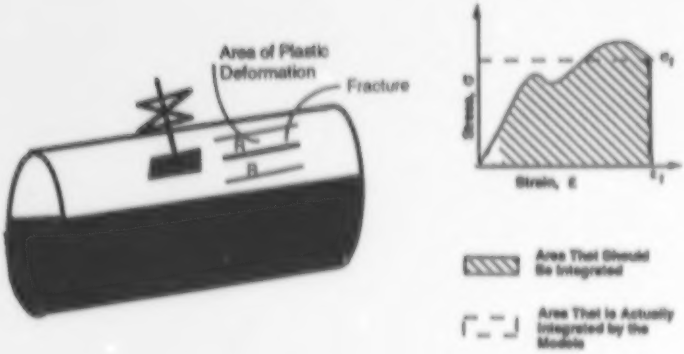
Area of Plastic Deformation
Fracture
B
B
Stress, σ
σ_f
Strain, ε
ε_f
Area That Should Be Integrated
Area That is Actually Integrated by the Models

Figure 2: Area and Energy of Plastic Deformation.

Critical Fracture Length

Fire engulfment of a PLG tank does not necessarily lead to a catastrophic failure and an explosion. In some cases the tank ruptures in the vapour space forming a *fish mouth* vent but otherwise remains intact [2, 13], whereas in other events the tank breaks into three or more pieces and a BLEVE results.

These phenomena lead us to hypothesize a *Critical Fracture Length*. It is defined as that length of fracture that, when exceeded, results in a complete disintegration of the container.

It is clear that the fracture propagation of a PLG tank commences in the vapour space, where the metal wall temperature is highest and the strength lowest. In contrast, the liquid wall temperature generally remains within a few degrees of the saturation temperature at the prevailing pressure. Both small scale and medium scale tests indicate that the difference in vapour and liquid wall temperatures can be as high as 600°C [6, 10]. If a fracture propagates (Figure 3) into the relatively cooler and, therefore, stronger liquid wall, two possibilities exist: the fracture may arrest or it may continue to propagate as a *brittle* fracture. The energy required for brittle fracture is much lower than that required for ductile or plastic failure therefore a fracture moving into a cooler wall invariably continues to propagate.

For the present analysis a critical fracture length l_f as shown in Figure 3 is used. If the estimated fracture length exceeds l_f, then there is a much higher probability of a catastrophic failure of the PLG tank.

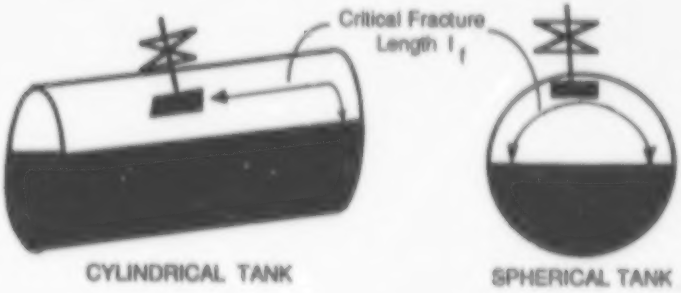

Figure 3: Critical Fracture Length.

Results

The hypothesis developed is applied to two cylindrical tanks of the dimensions given in Table 1. The rail tank is typical of railroad stock. The Railway Progress Institute and the Association of American Railroads (RPI-AAR) jointly conducted two full-scale tests using two test tanks built similar to a normal 128,000-liter rail tank car [17,18]. Of the two tests, the first was uninsulated; the second had an insulation layer of 3.2 mm (1/8 inch) applied on its exterior. Both cars were subjected to a pool fire fueled by JP-4. The uninsulated tank ruptured 24.5 minutes into the fire with an estimated 40%

volume fill of LP Gas still within the tank. The insulated tank had an estimated 2% volume fill remaining when it finally disintegrated after being exposed to fire for 94.5 minutes [17, 18].

Table 1.

Cylindrical Experimental Tank Characteristics

	Tank Dia. m	Tank Length m	Wall Thick. mm	Wall Temp. at Failure °C	Pressure at Failure kPa	Fill Level at Failure % vol	Catastrophic Failure
RPI-1*	3.0	18.3	15	450	1825	≈40%	YES
RPI-2*	3.0	18.3	15	450	1825	≈2%	YES
TC1**	0.61	3.35	6.4	---	1030	≈50%	YES
TC2**	0.61	3.35	6.4	580	1030	≈50%	YES

* Railway Progress Institute and American Railroads Association Tests [17,18].

** Vulcan Industrial Packaging Ltd. [19]

Figure 4 shows the estimated fracture or crack length as a function of liquid fill level (Curve a). The vapour wall temperature and the tank pressure used for this evaluation are from a RPI-AAR test and are given in Table 1. The critical fracture length resulting from the foregoing hypothesis is also shown in this figure.

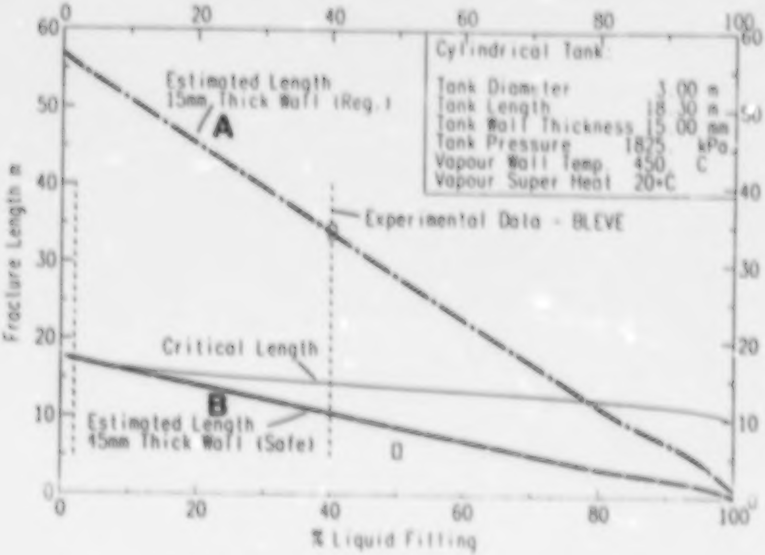

Figure 4: Estimated and Critical Fracture Length - Rail Tank Car.

Curve A and critical fracture length intersect at 78% fill level. This indicates that the liquid fill must be below 78% for complete disintegration of the container and therefore a BLEVE to occur. The two RPI-AAR test tanks BLEVEd with 40% and 2% fill levels, and are therefore consistent with the postulated hypothesis.

From the foregoing analysis it is possible to derive a tank car wall thickness, whose estimated fracture length is below the critical length for all fill levels. This is shown as Curve B in Figure 4. The wall thickness in this case is 45 mm, three times the thickness of a typical car.

Figure 5 presents the evaluated data for one fifth scale tests [19]. These tests were done in 1980 to study the feasibility of Explosafe® to control BLEVE. In all, six PLG tanks with propane were pool fire engulfed. Two out of the six were *benchmarks* without any Explosafe® and were named Baseline and Enigma. The Baseline failed catastrophically 9 1/2 minutes after fire engulfment [19]. Approximate measurements from photography shows a fracture length of 4 to 5 meters. The tanks were reported to be 50% full when failure occurred. The estimated fracture length (Figure 5) is therefore in good agreement with the experimental measurement. The Enigma test also failed with a fracture about one meter in length.

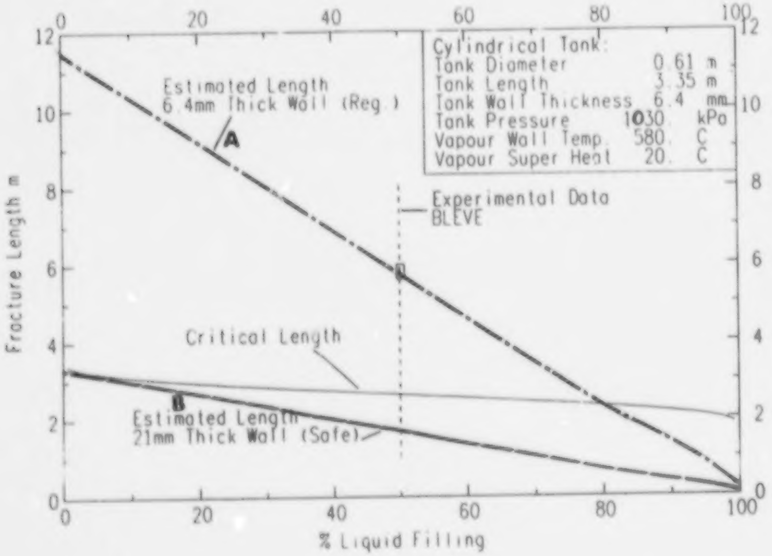

Figure 5: Estimated and Critical Fracture Length - One Fifth Tank.

The critical fracture length and the wall thickness required for sub-critical fractures is computed for the one fifth scale tank. The data are presented in Figure 5. Here too, the *safe* wall thickness is about 3 times that used.

Figures 6 and 7 give the estimated fracture length (Curve A), two sizes of spherical PLG gas tanks similar to those involved in the Mexico City accident [2,13], and an estimated *safe* fracture length (Curve B). Table 2 lists the known characteristics.

Table 2.

Spherical Tank Characteristics from
Mexico City Accident [2,13]

	Tank Dia. m	Wall Thick. mm	Wall Temp. °C	Pressure at Failure kPa	Fill Level at Failure % vol	Catastrophic Failure at Failure
F5/F6	16.5	37	450**	1030	~90%	NO
F1-F4	14.5	26	450**	1825	~50%	YES

The two larger vessels ruptured in the vapour space into *fish mouth* openings but did not disintegrate catastrophically [2]. Even though the exact fill level at the time of rupture is now known, the theory indicates that the tank would not have catastrophically ruptured above 58% liquid fill. Photographs of the tank during the accident, indicate a fish mouth rupture approximately 6 meters long on both vessels. From our hypothesis (Figure 6) this translates into about 87% filling, at time of rupture.

Initial tank liquid fill levels were stated to have been 90% filled. Similar to the cylindrical tanks a sub-critical tank wall thickness is computed and its fracture length variation with fill level is also shown in Figure 6.

Figure 7 shows the fracture length for the smaller tanks. All four of these disintegrated catastrophically. The figure indicates that this size is not stable below a 70% volume fill. Similar to the other spherical tank, the sub-critical tank wall thickness is evaluated as shown. The tank needs to have approximately double its wall thickness to achieve stability at all fill levels.

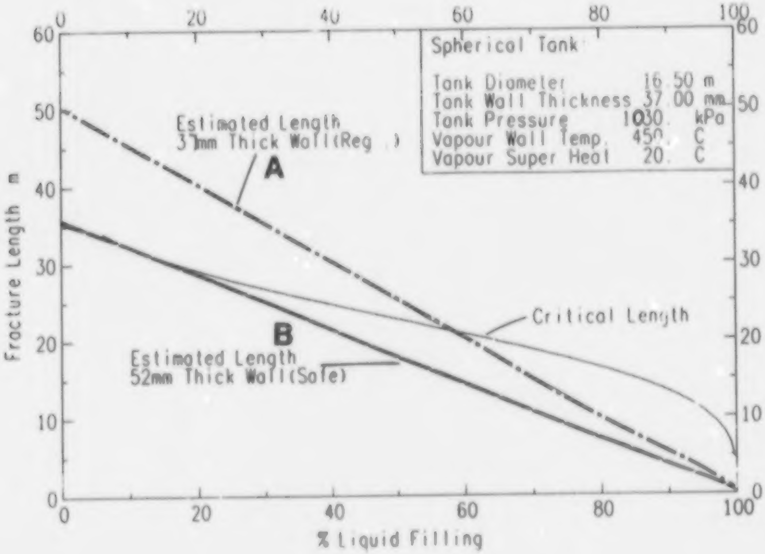

Figure 6: Estimated and Critical Fracture Length - Spherical Tank (Large).

Conclusions

The failure mechanism proposed in this paper indicates a number of areas for further research that will reduce the risk of catastrophic failure of PLG tanks. Evidence from accident and experimental data appear to provide support for the hypothesis. This mechanism does not however, provide an insight to some of the more violent explosions such as occurred in the 1984 accident in Mexico City.

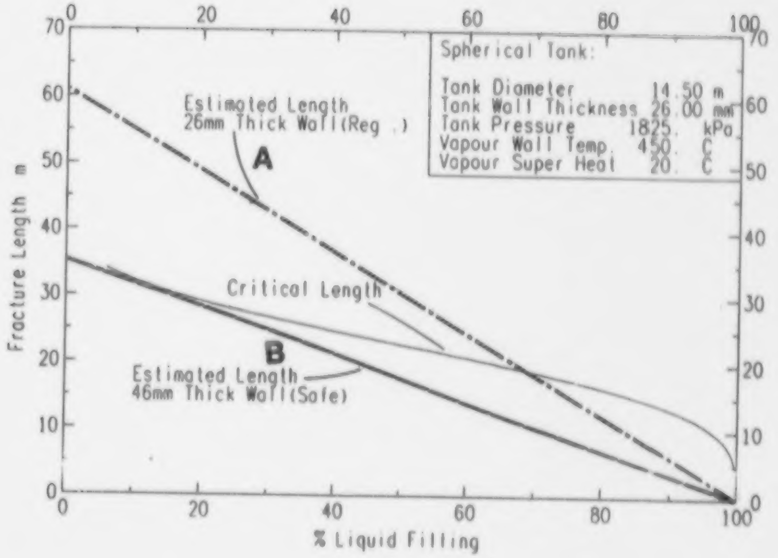

Figure 7: Estimated and Critical Fracture Length - Spherical Tank (Small).

Nomenclature

A_o - Tank wall cross-section area before any plastic deformation
A_f - Minimum wall cross-section area for tank integrity
C_p, C_v - Specific heat capacity of vapour at constant pressure and volume
D - Tank Diameter
I - Fracture length
I_f - Critical fracture length
E_f - Strain energy absorbed by plastic deformation during rupture
M_1 - Vapour space mass just prior to rupture
M_2 - Vapour space mass at atmospheric pressure
P_1,P_2- Tank pressure and atmospheric pressure
R - Tank radius

R_m - Gas constant
t - Tank wall thickness before rupture
V - Vapour space volume
W - Work done by expanding gas
Z - Compressibility factor
γ - C_p/C_v
σ - Tank wall stress
σ_f - Tank wall stress at failure

References

[1] Grange, S.G.M., Report on the Mississauga Railway Accident, Supreme Court of Canada, Toronto, Ontario, TP2223, 1983.

[2] J. Pietersen, C.M., Analysis of the LPG-disaster in Mexico City, J. Hazardous Materials, Amsterdam, The Netherlands, Vol. 20, 85-107, 1988.

[3] Anon, LP Gas Explosions A Case Study, National Fire Protection Association, No. 51-13, Quincy, Mass., 1974.

[4] Mudan, K.S., Hazard Ranking for Chemical Process Facilities, ASME Winter Annual Meeting, Boston, Massachusetts, 1987.

[5] Reid, R.C., Some Theories on Boiling Liquid Expanding Vapour Explosion, FIRE, pp. 525-526, 1988.

[6] Sumathipala, U.K., Thermohydraulics of an Externally-Heated Pressure-liquefied Gas Tank: An Experimental Study, Ph.D. Dissertation, University of New Brunswick, Fredericton, New Brunswick, 1990.

[7] Zuber, N., Problems in Modelling of Small Break LOCA in Heat Transfer in Nuclear Reactor Safety, ed. G.S. Bankoff and N. H. Adgan, Hemisphere, Washington, D.C., pp. 3-48, 1983.

[8] Smoglie, C., Two Phase Flow Through Small Banches in a Horizontal Pipe with Stratified Flow, Dissertation, University of Karlsruhe, West Germany (Kff 3861), 1984.

[9] Moodie, K., L.T. Cowley, R.B. Denny, L.M. Small and I. Williams, Fire Engulfment Tests in a 5-tonne LPG tank, J. of Hazardous Materials, Elsevier, Amsterdam, The Netherlands, Vol. 20, pp. 55-71, 1988.

[10] Moodie, K., K. Billings, H. Beckett and J.R. Griffiths, Total Pool Fire Engulfment Trials on a 5-tonne LPG Tank, Health and Safety Executive, Research and Laboratory Services Division, Harpur Hill, Buxton, Derbyshire (6 volumes), 1987.

[11] Tunc, M. and J.E.S. Venart, Incident Radiation from an Engulfing Pool Fire to Cylinder, Part II, Fire Safety Journal, Vol. 8, No. 2, pp. 89-96, 1985.

[12] Tunc, M. and J.E.S. Venart, Drudent Radiation from a Flare to a Horizontal a Horizntal Cylinder - Part I. Fire Safety Journal, Vol. 8, No. 2, pp. 81-88, 1985.

[13] Pieterson, C.M., Analysis of the LPG Incident in San Juan Ixhuatepec, Mexico City, TNO Report, Apeldoorn, Netherlands, Dossier 8727-13325, Ref. 85-0222, 1985.

[14] Baum, M.R., The Development of the Breach Generated by Axial Rupture of a Gas-Pressurized Steel Pipe, J. of Pressure Vessel Technlogy, ASME, New York, Vol. 104, pp. 252-261, 1982.

[15] Mann, Douglas, LNG Material & Fluids, A Users Manual of Property Data in Graphic Format, Cryogenis Division, Inst. for Basic Standards, NBS, Boulder, CO, 1977.

[16] McClintock, S.A., A.G. Argon, Mechanical Behaviour of Materials, Addison-Wesley, Reading, Massachusetts, pp. 571, 1966 .

[17] Manda, C.J., Phase II Report on Full Scale Tests, RPI-AAR TCRP report, Washington, D.C., Report No. RA-11-6-31 of December 12, 1975.

[18] Townsend, W.C., Anderson, J. Zook and G. Coguill, Comparison of Thermally Coated and Uninsulated Rail Tank Cars Filled with LPG Subjected to a Fire Environment, Federal Railroad Admin. Whitesand, New Mexico, Report No. PB241702, 1974.

[19] Appleyard, R.D., Testing and Evaluation of the Explosafe® System as a Method of Controlling the Boiling Liquid Expanding Vapour Explosion (BLEVE), Transport Canada Report No. TP 2740, 1980.

EXPERIMENTAL STUDY OF CHEMICAL BEHAVIOUR AT SEA :

POLLUTMAR III SEA TRIALS

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ABSTRACT

In order to better understand the behaviour of chemical when accidentaly released at sea, CEDRE has carried out offshore trials in October 1990 with the French Navy.

These experiments consisted in dumping different kinds of chemicals, dissolvers and floaters up to a volume of 1 m3 each.

The plumes of dissolved chemical were measured and recorded at 3 depths, while the vapor emission was followed using special sensor.

On floaters, the slick aeras were assessed using aerial remote sensing device as the Infra-Red Thermographies.

All data collected were useful to check the reliability of predicting models for spreading, evaporation and diffusion.

I. INTRODUCTION

A great many studies have been carried out in order to determine the behaviour of chemical substances when they are released at sea. However, most of these studies have been theoretical such as the prediction of behaviour based on calculations using computerized models which were previously developed up to this time.

Unfortunately, there has been very little experimental work done in situ, at sea, which will permit us to verify the reliability of the prediction models. For this reason, the French authorities have undertaken the Pollutmar Experimental Program which consists of testing in the open sea. This program has been accomplished with the help of technical advice from CEDRE and with the logistic support of the French Navy. In 1989, the sea trials POLLUTMAR took place, in order to observe the behaviour of floating and soluble substances at sea, and in 1989, POLLUTMAR II was concerned with the behaviour of gas clouds at sea.

In 1990, the sea trials (POLLUTMAR III) took place off the coast of Brittany (the Western coast of France) and consisted of releases between 400 l to 1 000 l of chemicals in order to specifically study :

1) The possibilities of using teledetection techniques in the event of chemical spills, especially the Infra-Red Scanner which is currently employed by French authorities.

2) The phenomena of Spreading, Evaporation and Dissolving for Floating and Soluble chemicals.

The observations made during this third phase of the study have also been compared with the predictions given by several computerized models in order to verify the models' reliability.

II. SEA TRIALS IN THE POLLUTMAR III PROGRAM

The sea trials took place in two distinct phases for this last chapter in the POLLUTMAR Experimental Program.

Phase 1 : Five releases of 1 m3 each (an oil, and two floating chemicals, which were both dyed and undyed) in order to study:

a/ teledetection (responses compared for the various chemicals, especially when using Infra-Red detection methods)

b/ evaporation/gas release

Phase 2 : Three releases of a colored soluble substance in order to observe its diffusion in water at various depths (1, 2, and 4 m).

III. TESTING METHODS

III. 1 - METHOD FOR RELEASING THE CHEMICALS

Each chemical slick was obtained by the instantaneous release of the substance to be studied, on the sea's surface. This release was possible since the substance was pumped into an open ended cylinder which, when raised, would instantly free the chemical. This method of release has the advantage of being able to be repeated in the same manner as often as necessary, and of creating slicks which are located exactly where desired.

III. 2 - PHASE 1 : COMPARISON AFTER RELEASE OF DIFFERENT FLOATING SUBSTANCES

Five slicks of 1 m3 each were successively released at very little distance from each other in order to compare their evolution (their slick formation and spreading), and the images obtained using teledetection devices, as well as to measure any vapor release in the air, for evaluation of the phenomenon of evaporation.

Three substances were chosen for this test phase :

a) diesel fuel, as a reference substance

b) ethyl-2-hexanol, a colorless floating chemical with a solubility of 0.1 % (classified as a floater/dissolver in the European Classification)

c) N-butyl methacrylate, a colorless floating/volatile chemical with a solubility of 0.6 % (classified as a floater/dissolver/evaporator in the European Classification).

The two chemicals (Ethyl 2-hexanol and N-butyl Methacrylate) were released with and without a dye (Organol Red) in order to verify if the dye has a particular influence on detection when using remote sensing devices.

The measures used in the teledetection were done on board an airplane using an Infra-Red Scanner (thermography) and a side scan radar apparatus (SLAR).

Any gas released in the air was measured using an HNU photo ionization detector, and a Bruel Kaer detector (involving an Infra-Red photo-acoustic detection method).

The slick spreading was observed and evaluated on the basis of photographs (for the dyed slicks) and using the thermographic images obtained by means of the Infra-Red detector.

III.3 - PHASE 2 : OBSERVATION OF DIFFUSION DISSOLVING OF A SOLUBLE SUBSTANCE AT SEA

Three releases of 400 and 800 l of isopropanol took place. The isopropanol was traced with a water soluble dye (Rhodamine B, 8g/l).

The choice of this dye was made after laboratory testing, on a smaller scale, revealed that the behaviour of a mixture of isopropanol + Rhodamine B was identical to the behaviour of an undyed isopropanol.

The diffusion of the isopropanol at sea was continually measured using spectro fluorometric measurements for the content of colorant at depths of 1 m, 2 m, and 4 m.

Simultaneously to the spectro fluorometric measuring, water samples were recovered which enabled a later laboratory verification that the amount of colorants and isopropanol remained in the same original proportion during the entire test period.

All the measuring set-up (which included a submerged pump, and a spectro fluorometer connected to a recording device for each depth to be measured) was installed on a small craft, in order to cause the least disturbance to the chemical slick during the period necessary to complete the measurements.

During the entire test period, the small sea craft crossed the slick several times in order to obtain the necessary profiles of the Rhodamine B concentrations. As far as possible, these crossing were marked in relationship to the slick (on sketches and on the photographs taken from a helicopter) in order to locate the concentration profiles on the actual slick. An example of a concentration profile and slick crossing is shown on further Figure 2 .

IV. OBSERVATIONS AND RESULTS

IV.1 - TELEDETECTION

The Infra-Red thermographs have enabled us to detect releases of methacrylate, however the images have less distinct contrasts than those taken for the diesel oil. Nevertheless, the image is of a good quality, and the methacrylate images are similar despite whether the chemical is dyed or undyed.

No I.R. detection was possible for the release of Ethyl-2-Hexanol (either dyed or undyed).

For the side scan radar equipment (SLAR), no detection was revealed for any of the three types of substances released (diesel oil, methacrylate, or ethyl-2-hexanol) however, considering that this type of detection is more long range, the size of the spill, even if as much as 1 m3, may have been insufficient to be viewed by this type of large range imagery.

IV. 2 - SPREAD OF FLOATING SUBSTANCES

Observations have shown that :

1. The diesel oil slick is considerably spread in the wind direction (3000 m2 five minutes after release) but becomes relatively more compact at the end of 1 h 30 to cover about 1,800 m2 in the shape of a slick 80 x 250 m.

2. The slick of methacrylate without dye had a more stringy appearance and its surface diminished from the 2,200 m2 observed 5 minutes after release to a surface of 1,400 m2 at the end of 40 minutes (Figure 1).

3. The slick of dyed methacrylate is broken up and is also reduced from a surface of about 4,300 m2 after 5 minutes following the release to about 1,200 m2 after 40 minutes following the release.

Figure 1

Evolution of the Slick of Undyed N-butyl Methacrylate

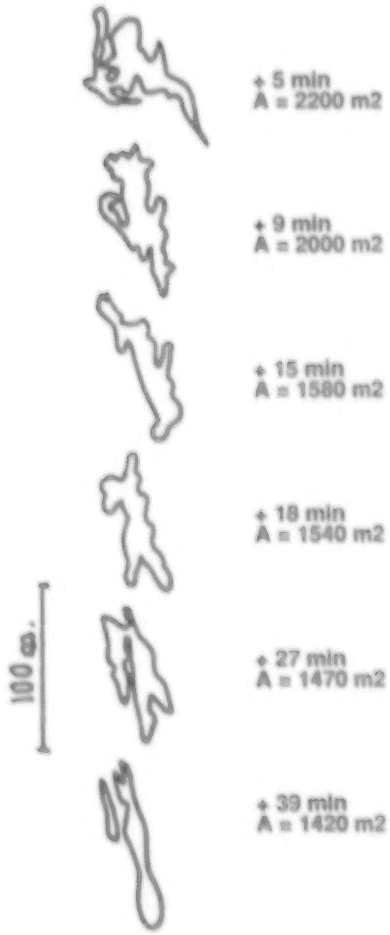
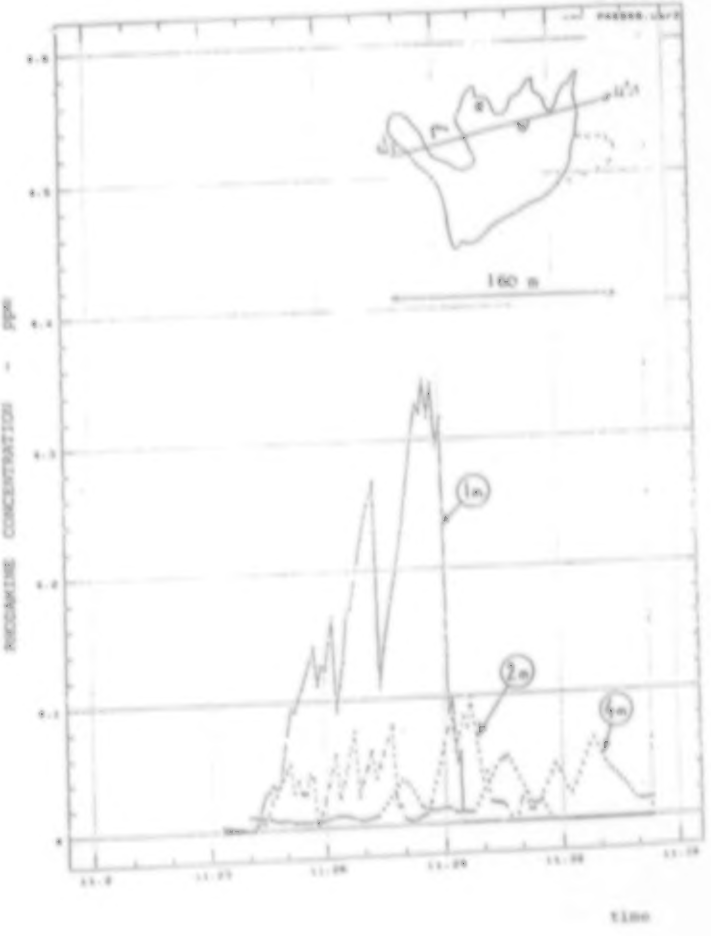

+ 5 min
A = 2200 m2
+ 9 min
A = 2000 m2
+ 15 min
A = 1580 m2
+ 18 min
A = 1540 m2
100 m.
+ 27 min
A = 1470 m2
+ 39 min
A = 1420 m2

Figure 2
Evolution of the profile concentration Eight Crossing of Slick n°9



The fact that the slick of dyed methacrylate was half as much spread out in the first few minutes following the release as the slick of undyed chemical may be due to the difference in the two spreading coefficients which varied between 17 to 24 when previously measured in the laboratory.

For the slick No. 4 (dyed methacrylate), the aerial photographs confirm the images received by the I.R. thermographic imagery, and show a slick size which is reduced by half 40 minutes after release.

This reduction in the size of the slick for the two slicks of methacrylate is due to the chemical's evaporation rate.

IV.3 - EVAPORATION

- For the ethyl-2-hexanol the concentration of the gas released in the air down wind from the slick, shortly after the chemical slick release, was measured as being between 1 and 5 ppm, with a maximum concentration of 10-15 ppm. The evolution of the gas concentrations is not very regular and corresponds to the successive puffs of wind where the chemical concentrations were cut by passages of practically pure air.

After 53 minutes following the initial release, we can still measure a certain amount of evaporation. To give an idea of what we expected when comparing the real concentrations with those proposed by a prediction model, the model CHEMSPILL predicted that the slick would be completely evaporated after 23 minutes.

- For the methacrylate, gas concentration profiles were made at various distances from 50 meters down wind from the slick up to a distance of 250 meters. The slick disappears about 50 minutes after the release (the CHEMSPILL model predicted this would take place after 28 minutes). The following table shows the gas concentrations in function of the distance involved.

Dist. (m)	Profil 1 (10 mn)	Profil 2 (15 mn)	Profil 3 (25 mn)	Profil 4 (35 mn)
50	35.00	26.7	27.2	26.8
100	30.00	15.0	13.00	9.00
125	28.00	11.0	10.0	7.5
150	25.0	10.0	7.00	6.5
175		9.5	6.4	5.5
200		6.0	4.5	4.3
250	4.0	4.8	1.6	1.5

Table 1

Other gas concentration measurements were made for the release of isopropanol (phase 2 of the Sea Trials) and have shown that in the case of a soluble chemical, evaporation takes place much more slowly (gas concentrations in air of 1 to 4 ppm as much as 4 hours after the initial chemical release).

This observation is very different from what was predicted by the models (CHEMSPILL) where a rapid rate of evaporation (with concentrations from 40 to 50 ppm) were predicted for only the first three minutes.

The phenomenon of evaporation for soluble substances still needs to be evaluated.

IV. 4 - RATES OF DISSOLVING/DIFFUSION FOR SOLUBLE SUBSTANCES IN THE SEA

IV.4.1. Heterogeneity of the Dissolved Clouds Released by a Dissolving Chemical

An examination of the concentration profiles for the isopropanol when it is dissolved in seawater has shown that even though the slicks are compact very shortly after the isopropanol is released, within a few minutes the slicks begin to break up into several smaller, stringy slicks ; therefore the concentration profiles of dissolved chemical are very irregular (a succession of peaks) (see Figure 2).

IV.4.2. Rate of decreasing concentrations is a function of the sea surface agitation (Figure 3).

If the sea is relatively agitated (with waves 1.5 m high, for the release of 800 l of isopropanol slick n°10), after 45 minutes there is no more than a few ppm of isopropanol at a depth of 1 m.

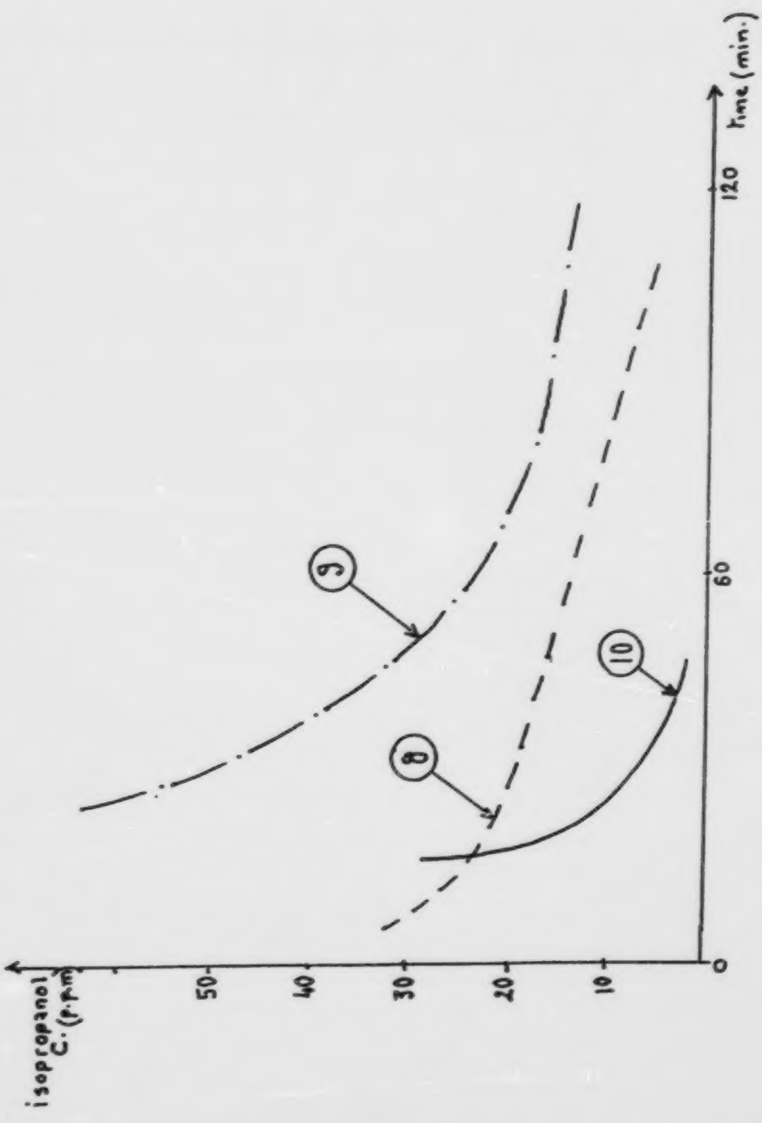
If the sea is calm (as was the case for the two other isopropanol releases of 400 l each slicks n°8 and 9), the dilution was much slower, and it was necessary to wait for 2 to 3 hours before a concentration of only a few ppm could be achieved.

A comparison of two different sea state agitations can be made by comparing the concentrations for slicks 9 and 10 where it can be seen that 30 minutes after release at a depth of 1 m, the concentrations of slick 10 are 10 times lower that those observed for slick 9.

IV.4.3. Evolution of a dissolved chemical depends on the state of the sea's agitation.

a/ on calm sea such as was present for the release of slick first isopropanol slick (400 l), the peaks of concentration at 2 m depth remained low and constant (few ppm) even when the

Figure 3
Evolution of the peaks of concentration at level 1 for Slick n° 8, 9 and 10



concentrations recorded on the surface showed large variation ; this shows that under these particular sea conditions, the diffusion of a chemical is more horizontal than vertical, and the chemical is more rapidly disseminated over the surface.

b/ for agitated sea such as the conditions at the time of release last isopropanol slick (800 l), the peaks of concentration at 2 and 4 m depths are only slightly different from the values obtained at 1 m depth ; this suggests that the vertical diffusion, at least up to a depth of 4 m, was much more significant than for the previous case, and had as much effect as the horizontal diffusion. The turbulence caused by 1.5 m waves has affected the diffusion for a depth of at least 4 m.

For a calm sea state, the predictions proposed by the CHEMSPILL model were very close to what was actually observed (see Figures 4 and 5).

V. CONCLUSIONS

The POLLUTMAR III sea trials have provided a great deal of information concerning the behaviour of chemicals released at sea. The objectives of the study were achieved, especially as far as :

1/ a teledetection of floating chemical substances : the significance of the equipment used by French authorities has been confirmed, but the limitations of this equipment have also been shown. In the future, it will be necessary to prepare a list of the floating chemicals which are able to be detected using this type of equipment.

2/ a better understanding of the behaviour of chemicals released at sea in terms of their evaporation and dissolving; one important aspect of this study concerns the numerous measurements that were made which have enabled us to verify the propositions of certain prediction models available at this time.

As far as the phenomenon of evaporation, the models need to be improved, especially in order to take into consideration the simultaneous actions of evaporation and dissolving.

As far as dissolving is concerned, the models seemed to be in agreement with the observations made in the field which is encouraging. Nevertheless, it will be necessary to confirm these findings under different conditions (more agitated sea state, or when testing other chemicals) in order to completely verify the reliability of the predictions calculated by the models.

Figure 4
Slick n°8 : Evolution of the peaks of concentration observed (O) compared to the predicted peaks of concentration (P)

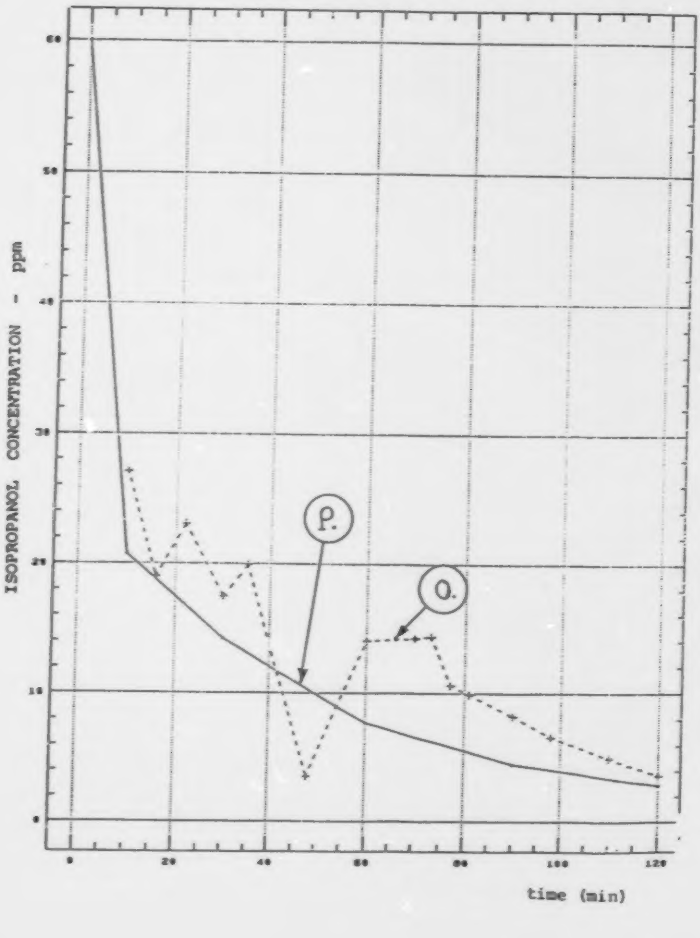
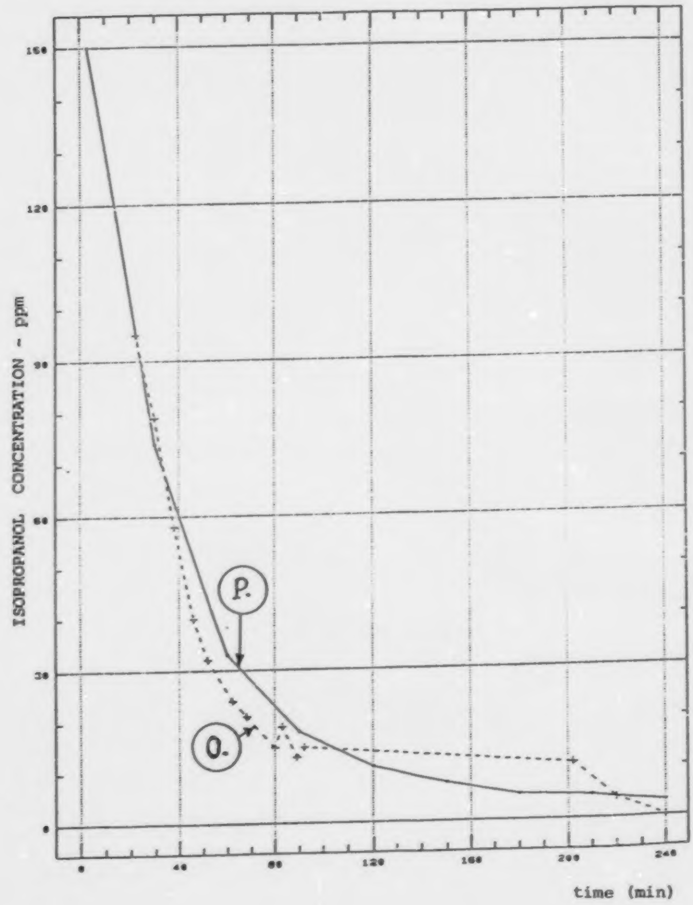


Figure 5
Slick n° 9 : Evolution of the peaks of concentration observed (0) compared to the predicted peaks of concentration (P)



Use of Carbon Dioxide to Control the pH of Alkaline Effluents Discharging to Receiving Streams

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INTRODUCTION

Carbon dioxide is present in the atmosphere and ranges in concentration from 0.03-0.05%. It occurs naturally from the respiration of animal life and the degradation of organic matter. Its concentration in the atmosphere has been rising, mainly as the result of combustion of fossil fuels.

Carbon dioxide is a normal component of all natural waters, the source being the CO_2 contained in the atmosphere that is readily soluble in water. At a concentration of 0.03% in the atmosphere, the equilibrium solubility is about 0.45 mg/l [1]. Natural waters also contain carbon dioxide in the combined state, in the form of carbonates and bicarbonates.

Because of this presence in natural waters carbon dioxide, when used for neutralizing alkaline waste streams, does not impose any extra environmental stress on the receiving stream.

This paper describes how carbon dioxide is used to lower the pH of effluents that are discharged accidentally or in a controlled manner into a receiving stream.

Properties of CO_2

Carbon dioxide is a non-flammable colourless, odourless gas that has a slightly acidic taste when dissolved in water. It is quite soluble in water [2] as shown by Table (1).

Table (1) Solubility of CO_2 in tap water at pressure 101 KPa

Temperature	Solubility
°C	g/l
10 20 30	2.40 1.69 1.29

At 25°C a saturated solution has a pH value = 3.8.

Its density is about 1.5 times heavier than air, with a threshold limit value of 5000 ppm. Because of this, if carbon dioxide is used in confined spaces, it is important to have a good ventilation system to avoid accumulation at the lowest elevation levels.

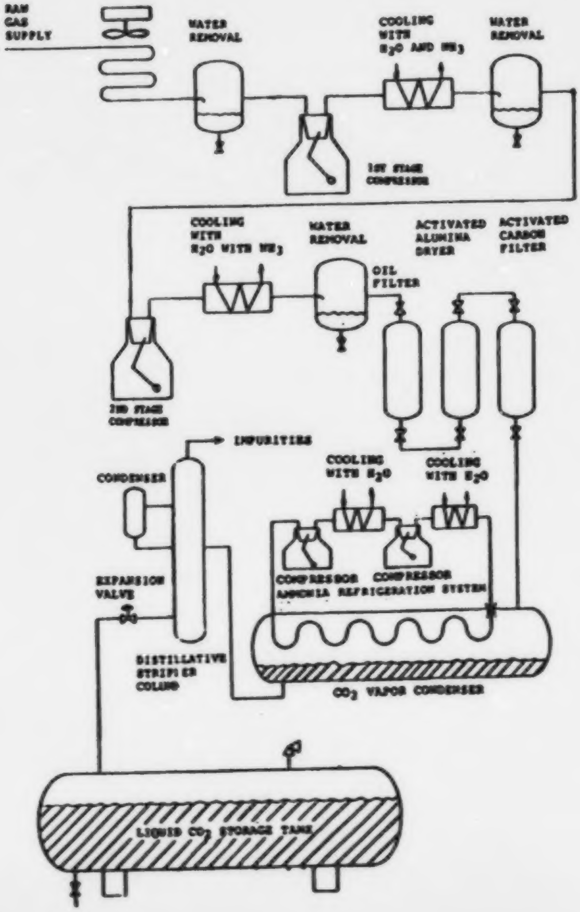
Its triple point is -56.6°C at a pressure of 416.5 KPa gauge. It is normally stored in the liquid state at a temperature of -20°C and a pressure of 2000 KPa.

Production

Carbon dioxide is not manufactured as such, but is recovered from industrial operations. The most important sources of raw carbon dioxide are Fertilizer Manufacture, Fermentation Processes, Chemical and Petrochemical Operations.

A typical flowsheet for recovering and purifying carbon dioxide is shown in Fig. (1). The raw source is first compressed after which it is cooled to remove water, then it passes to a second stage compressor. Further cooling removes more water followed by oil removal in a filter, further drying in an activated alumina dryer and finally odour and objectionable taste removal using an activated carbon filter. It is then cooled and liquified before passing into a distillation-stripping column where non condensables are removed. Finally it is expanded through an expansion valve where it condenses as a liquid in a storage tank.

Fig. (1) Carbon Dioxide Production

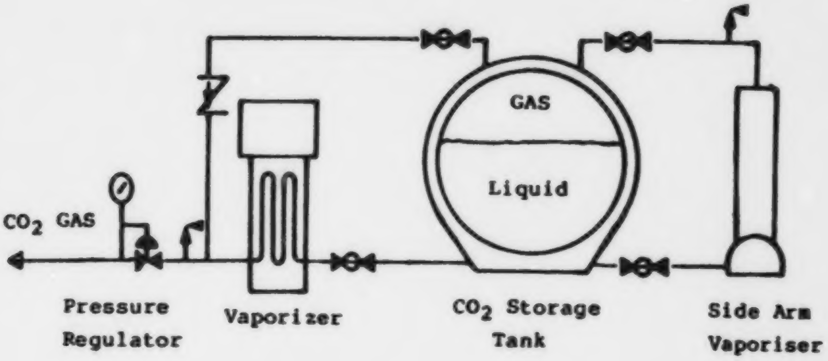

RAW GAS SUPPLY
WATER REMOVAL
COOLING WITH H_2O AND NH_3
WATER REMOVAL
1ST STAGE COMPRESSOR
COOLING WITH H_2O WITH NH_3
WATER REMOVAL
ACTIVATED ALUMINA DRYER
ACTIVATED CARBON FILTER
OIL FILTER
2ND STAGE COMPRESSOR
IMPURITIES
CONDENSER
COOLING WITH H_2O
COOLING WITH H_2O
EXPANSION VALVE
COMPRESSOR
COMPRESSOR
AMMONIA REFRIGERATION SYSTEM
DISTILLATIVE STRIPPER COLUMN
CO_2 VAPOR CONDENSER
LIQUID CO_2 STORAGE TANK

Storage & Usage

Liquid Carbon dioxide is pumped into Tank Trailers at a pressure of about 1500 KPa gauge. It is then transported to a customer location where it is loaded into a Storage Tank. Here it is maintained at a pressure of about 2000 KPa gauge and temperature of about -20°C by a side arm vaporizer that takes liquid and turns it into gas.

At low flowrates gas is withdrawn from the head space. At higher flowrates liquid carbon dioxide is withdrawn from the bottom of the tank and vaporized by an electrically operated vaporizer as shown in Fig. (2).

Fig. (2) Carbon Dioxide Storage and Usage


GAS
Liquid
CO_2 GAS
Pressure Regulator
Vaporizer
CO_2 Storage Tank
Side Arm Vaporiser

Carbon Dioxide as a Neutralizing Agent

The traditional method of neutralizing an alkaline waste water is to use sulphuric acid. However, this is not the safest chemical to use because it causes severe burning if exposed to the skin. Further, sulphuric acid is very corrosive and special materials of construction are required to transport and handle it.

Carbon dioxide can be used as a substitute for sulphuric acid and it is at least equally, if not more, cost effective.

Carbon dioxide forms a weak acid with a low ionization constant when dissolved in water. [3]

$$CO_2 + H_2O = H^+ + HCO_3^-$$

This further ionises but more weakly than the first

$$HCO_3^- = H^+ + CO_3^-$$

This weak acid reacts with caustic as follows

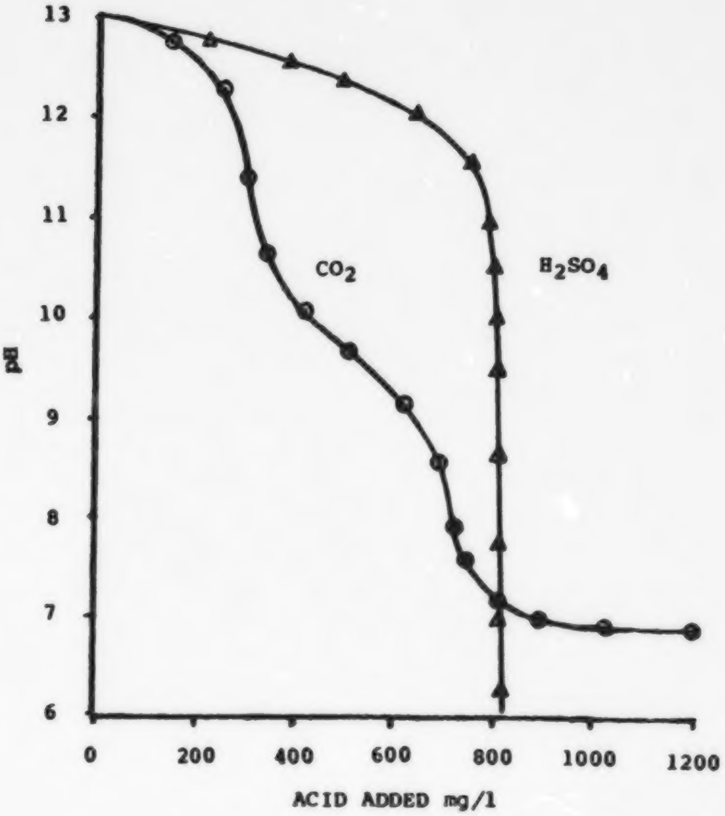
$$2\ NaOH + CO_2 + H_2O = Na_2CO_3 + 2\ H_2O$$

As more CO_2 is added, there is further reaction

$$Na_2CO_3 + CO_2 + H_2O = 2\ NaHCO_3$$

The curves in Graph (1) show a solution of caustic soda about 0.1 M in concentration titrated against carbon dioxide and sulphuric acid.

GRAPH (1) NEUTRALISATION OF CAUSTIC SODA SOLN



Initially the consumption of sulphuric acid on a weight basis exceeds that of carbon dioxide for the same pH change. This difference narrows as the pH falls until at about pH = 7, the consumption of acids is about the same.

Below pH = 7, sulphuric acid lowers the pH rapidly for small additions whilst carbon dioxide changes the pH slowly for large additions.

Hence these curves indicate two advantages for the use of carbon dioxide.

(1) the CO_2 consumption down to about pH = 7 is less than or equal to sulphuric acid.

(2) at pH = 7 a large addition of carbon dioxide makes small changes to the pH, so that "overshooting" of pH is not possible.

Description of Applications of Carbon Dioxide as a Neutralizing Agent

Caustic Spill into an Effluent Treatment Process.

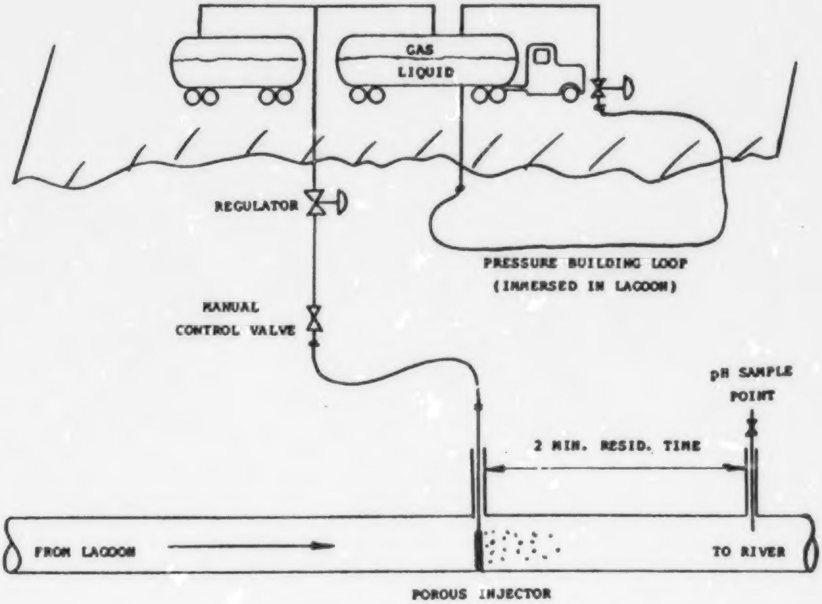
This occurred in a Pulp Mill that accidentally dumped a large volume of strongly caustic liquor into the Wastewater Treatment Process. This immediately raised the pH of the process to greater than 10 and forced the Mill to shut down to prevent effluent flowing into the river.

The Mill had begun sulphuric acid addition to the lagoon but because of its huge size, it was found that there was poor mixing and the pH of the effluent discharging would have exceeded the permit restrictions.

It was determined that if carbon dioxide was added to the effluent, the pH could be reduced to a level to allow discharge to the river thus enabling the flow to the lagoon to be restarted to keep the biomass active. Further, because of the buffering effect of the alkali an overdose of carbon dioxide would not drive the pH too low.

Hence a tank truck of liquid carbon dioxide was immediately dispatched to the site and set up to supply gas for dissolution in the effluent as shown in Fig. (3).

Fig. (3) Carbon Dioxide added to effluent from Wastewater Treatment Process.


GAS
LIQUID
REGULATOR
PRESSURE BUILDING LOOP
(IMMERSED IN LAGOON)
MANUAL
CONTROL VALVE
pH SAMPLE
POINT
2 MIN. RESID. TIME
FROM LAGOON
TO RIVER
POROUS INJECTOR

The discharge from the lagoon to the river was through a pipe 90 cms in diameter and about 3.5 km long. It was decided to dissolve the carbon dioxide in this pipe because the conditions were more favourable than attempting to do it in the lagoon. Hence a diffuser was installed in the pipeline close to the outflow of the lagoon. Carbon dioxide liquid was drawn from the trailer and vaporized using a hose immersed in the lagoon, thus building up a gas pressure in the head space. The gas was metered to the diffuser by a manual valve, and it was dispersed and dissolved in the flowing effluent. At a distance of about 100 m downstream from the diffuser, the pH was measured and the carbon dioxide flow adjusted to obtain pH = 7-8.

All this was accomplished within 24 hours of receiving a request for carbon dioxide, and it allowed the Mill to restart the process about 2 days earlier than planned.

Caustic Spill into a Waste Treatment Process

This was a case similar to that previously described in which caustic accidentally flowed into the treatment lagoon raising the pH to greater than 10. Sulphuric acid was immediately added to the inlet of the process, but because of poor mixing and the fear of making the process too acid, the pH remained alkaline.

It was decided to add carbon dioxide directly to the lagoon, close to the outlet to lower the pH to the range 7-8.

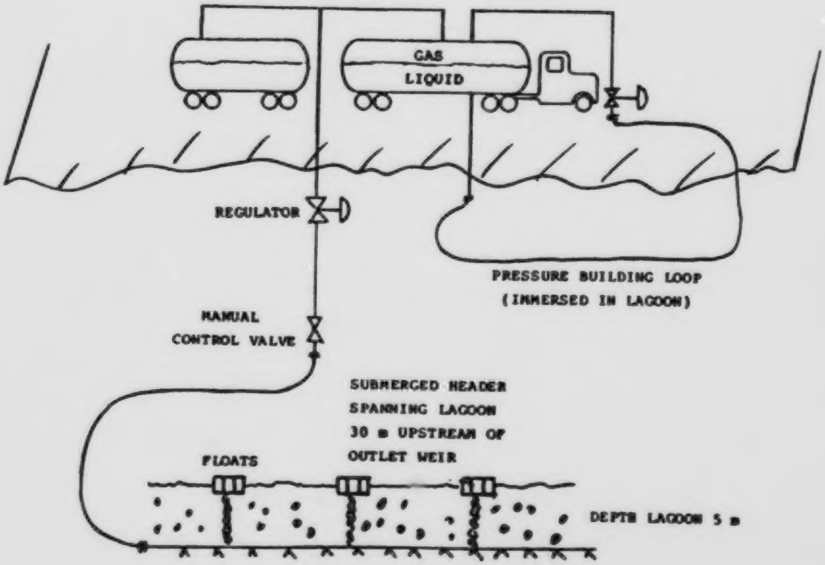
A truck with two trailers of liquid carbon dioxide was immediately dispatched to the customer's site. The trailers were hooked up to vaporize liquid into gas and to deliver this to the lagoon as shown in Fig. (4).

The liquid was vaporized by using about 30 m of hydraulic hose submerged in the lagoon with a pressure building regulator on the gas return to the head space of the trailers.

Carbon dioxide gas taken from the head space was added to the lagoon by a 30 m long header that was strung across the lagoon. This header was 5 cms in diameter and was drilled with 120 holes each about 2 mms diameter. It was suspended by means of floats so that the header was about 4 m below the surface. The flow of carbon dioxide was manually regulated, and the pH of the effluent lowered to 7.5.

This prompt action was accomplished within a period of 36 hours and ensured that the Mill met the pH permit restrictions without the need for shutting down.

Fig. (4) Carbon Dioxide added to Waste Treatment lagoon

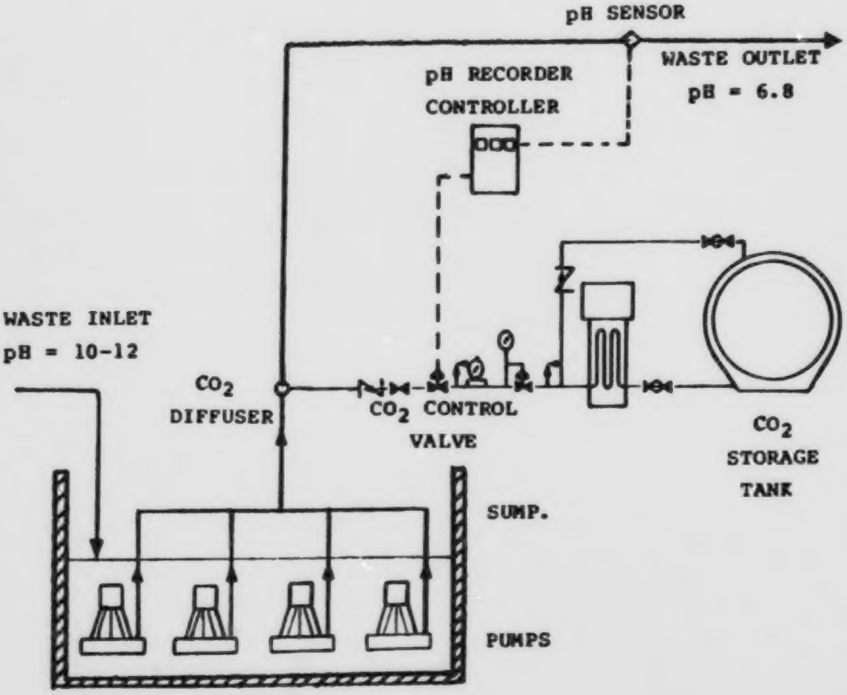

GAS
LIQUID
REGULATOR
PRESSURE BUILDING LOOP
(IMMERSED IN LAGOON)
MANUAL
CONTROL VALVE
SUBMERGED HEADER
SPANNING LAGOON
30 m UPSTREAM OF
OUTLET WEIR
FLOATS
DEPTH LAGOON 5 m

Regulated pH Control of an Alkaline Waste Stream

In this process an alkaline waste stream is reduced in pH from 10-12 down to 6.8 before it passes to a clarifier and subsequently a receiving stream. The process flowsheet is shown in Fig. (5).

The alkaline waste varies in flow from 90 m^3/hour to 900 m^3/hour and is collected in a sump and from here it is pumped out to maintain a constant level. To cope with the variable flow, between one and four pumps can operate for a flow of up to 900 m^3/hour.

Fig. (5) Regulated pH Control of an Alkaline Waste Stream


pH SENSOR
WASTE OUTLET
pH = 6.8
pH RECORDER
CONTROLLER
WASTE INLET
pH = 10-12
CO2
DIFFUSER
CO2 CONTROL
VALVE
CO2
STORAGE
TANK
SUMP.
PUMPS

The pumps discharge into a pipe 40 cms in diameter where the CO_2 is added through a diffuser. It dissolves in the waste stream under highly turbulent conditions and lowers the pH. The pH of the stream after CO_2 addition is monitored by a probe, and this signal feeds back to a recorder and controller that adjusts the flow of CO_2 by an automatic valve, to obtain the required pH target.

In this way it is possible to control the pH to a range of 6.8 ± 0.2.

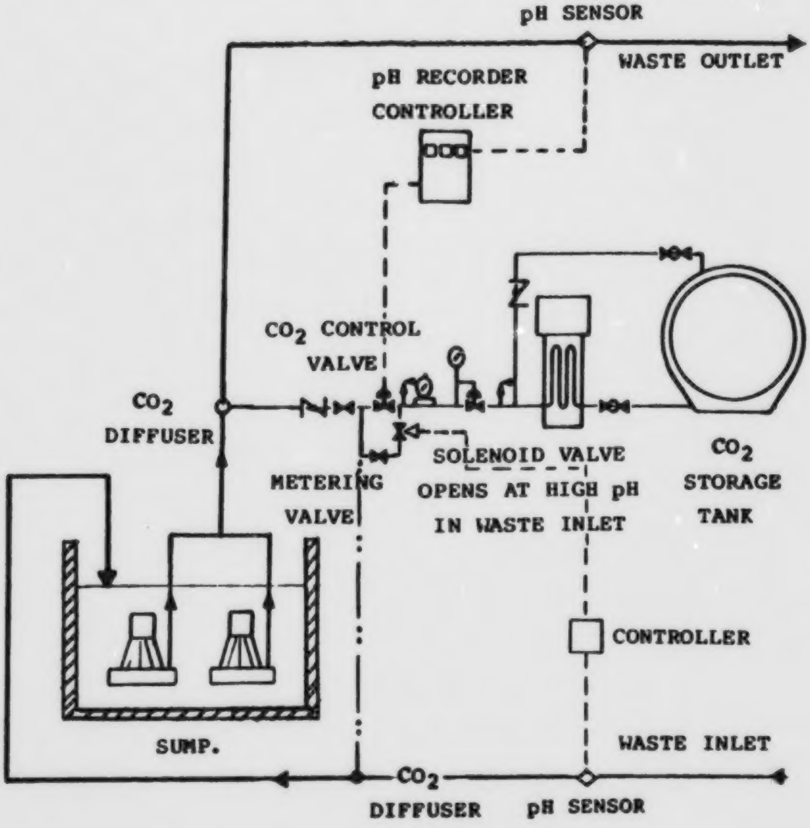
pH control of effluent with wide swings in carbon dioxide demand.

This case demonstrates a method of controlling effluent pH when process changes cause sudden swings in the carbon dioxide demand. Most control systems adjust the pH by adding acid based on the signal from a pH sensor on the final effluent. This can cause fluctuations in the final pH as a result of overdosing or a lag in the response of the instruments.

Canadian Liquid Air has devised a control system using carbon dioxide that adjusts the gas flowrate as a result of the input from two pH sensors as shown in Fig. (6). A pH probe senses the incoming pH and sets up an injection of carbon dioxide before the high pH flow reaches the injection point. This addition of about 50% of the required carbon dioxide flow prevents high pH effluent from discharging from the process. A second pH probe on the final effluent adjusts the carbon dioxide flowrate to meet the required limits of the effluent stream.

Thus the selection of carbon dioxide as the neutralizing acid prevents overshooting the reqired pH, and the measurement of both the incoming and final pH prevents undershooting and the discharge of effluent outside the permit pH requirements.

Fig. (6) **Control of pH for effluent having wide swings in carbon dioxide demand.**


pH SENSOR
WASTE OUTLET
pH RECORDER CONTROLLER
CO_2 CONTROL VALVE
CO_2 DIFFUSER
METERING VALVE
SOLENOID VALVE OPENS AT HIGH pH IN WASTE INLET
CO_2 STORAGE TANK
CONTROLLER
SUMP.
WASTE INLET
CO_2 DIFFUSER
pH SENSOR

Summary

This paper shows how carbon dioxide can be used to lower the pH of alkaline discharges that are either accidentally spilled, or discharged in a controlled manner.

Carbon dioxide is a safer neutralizing agent to use than sulphuric acid, and is not so corrosive requiring only the more common materials of construction for handling and storage.

Carbon dioxide is a weak acid and is buffered around pH = 7, so the risk of over-acidification is eliminated.

Carbon dioxide in neutralizing alkaline effluents, produces no sulphates, only carbonates and bicarbonates that are environmentally compatible with receiving streams.

Carbon dioxide can be quickly and easily transported to deal with any situation emergency or otherwise. When used in the gaseous form it does not require special equipment or pumps.

Liquid Air is responding to increasing pressures on industry to improve effluent quality and is working hard to develop new refinements in waste treatment. Our team of Engineers and Chemists will tailor solutions to your needs.

References

[1] Sawyer and McCarty, Chemistry for Sanitary Engineers, McGraw-Hill, 1967.

[2] L'Air Liquide, Gas Enclyclopaedia, Elsevier Scientific Publishing Company, 1976.

[3] Fair, Geyer, Okun, Water Purification and Wastewater Treatment and Disposal, Vol. 2, John Wiley, 1968.

DECONTAMINATION OF A MAJOR MERCURY SPILL SITE

by

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Introduction

Use of metallic mercury, even in relatively small quantities, can lead to extensive contamination if inadequate workplace controls are in use. In 1989, a spill of mercury was reported in the Wheelhouse of a dredge vessel. Subsequent investigation demonstrated airborne mercury vapour levels in excess of those expected for the size of the spill. Further investigation found mercury contamination throughout the Wheelhouse, in the boat deck below, and in lesser amounts in cabins, the mess and the galley.

The workplace environment was unacceptable, resulting in both excessive airborne mercury levels and direct exposure through surface contact. Mercury decontamination of the Wheelhouse necessitated complete removal of all interior structural components and asbestos insulation, as well as thorough cleaning and encapsulation of all underlying metal surfaces. Other areas of the vessel required less extensive decontamination.

The rational for asbestos removal in this situation was not the present or future risk of asbestos exposure, but massive contamination of the asbestos by mercury. If left in place, the asbestos would continue to act as a mercury source leading to ongoing air contamination. Disposal of waste asbestos through normal regulated landfill was not acceptable and alternate disposal options were required.

This paper will discuss the decontamination process including the removal of mercury contaminated asbestos. Some aspects of the asbestos removal work differed from those normally encountered by asbestos removal contractors.

Background

Over some 28 years, a Ship's Wheelhouse had become contaminated with mercury. The source of the mercury was two drag arm gauges filled with liquid mercury. These gauges were used to show the depth of dredging equipment. Uncontrolled discharge of mercury from the gauges and retopping resulted in the accumulation of large quantities of mercury in the Wheelhouse. An estimated 15 Kg of mercury had been spilled. Over this time period, clean-up of spilled mercury was haphazard, resulting in the retention of some 9 Kg of mercury at the base of the bulkheads and under consols and other equipment.

At the time of our investigation of this worksite in the Spring of 1989, measured airborne concentrations on mercury in the Wheelhouse exceeded 0.05 mg/m^3. This is unacceptable and a decision was made to thoroughly decontaminate the Wheelhouse and all other affected areas of the vessel. Surface sampling for mercury demonstrated that all surfaces in the Wheelhouse and other affected areas, including the boat deck immediately below the Wheelhouse, were contaminated. The process by which mercury spilled on a floor can contaminate bulkheads, deckheads and all equipment can be described as vaporization and condensation during heat-cool cycles, occurring daily, with the result over 20 years of complete contamination of all surfaces. This process, however, also resulted in penetration of mercury vapour into all porous surfaces including structural wood sheeting, bulk asbestos insulation and metal surfaces.

In addition to mercury contamination in the Wheelhouse, leakage through cable runs resulted in similar contamination of insulation in the boat deck ceiling. Mercury was also tracked on footwear from the Wheelhouse and boat deck to the main deck below, resulting in significant but less serious contamination of sleeping cabins, the mess and galley areas. Decontamination of the vessel required, therefore, a systematic approach to ensure that areas, once cleaned, did not become recontaminated.

Our experience of over 10 years of cleaning mercury-contaminated workplaces suggested that all materials in the contaminated areas would require individual cleaning, or removal where cleaning was not possible. The task of surface decontamination was assigned to the Ship's crew. These workers were instructed in the hazards of mercury, personal protective equipment needs, and work practices. Once movable items were removed from the Wheelhouse and boat deck an asbestos removal contractor was selected to remove and store the mercury-contaminated asbestos.

Mercury Health Hazards

There are two principal routes by which mercury exposure can occur. The first and most often recognized is airborne exposure to mercury vapour. The second is ingestive exposure resulting from food contamination, or hand-to-mouth contact following the touching of contaminated surfaces or tools. Both routes of exposure can result in accumulation of mercury in the body, primarily in the central nervous system. (1)

The accepted maximum exposure limit for regular airborne exposure to mercury vapour is 0.05 mg of mercury/m^3 of air (mg/m^3). A short term exposure limit of 0.15 mg/m^3 is commonly accepted. It is known that with extended uncontrolled exposures at 0.1 mg/m^3 exposed persons will start to exhibit signs of chronic mercury exposure. Signs and symptoms of chronic exposure include kidney damage, nerve damage, and psycho-social difficulties resulting from central nervous system injury. Gum disease is also a common early sign of chronic mercury exposure.

Acute exposures to higher concentrations of mercury can result in irritation of the eyes, cough, chest pain, difficulty in breathing and other systemic injury. An exposure of 1.0 mg/m^3 could pose serious potential for acute injury. Mercury vapour has no odour.

Clean-up and Disposal Criteria

There is no published criteria for acceptable surface contamination by mercury. Our experience has demonstrated that a surface contamination of less than 125 micrograms per metre squared surface area (125 μg/m^2) controlled body accumulation of mercury. The basis for proposing this level of acceptable surface contamination is twofold:

- surfaces contaminated at less than this level do not release sufficient mercury vapour to significantly contaminate the adjacent air;

- workers handling equipment and touching these surfaces do not exhibit increased urine mercury concentrations.

There are no international standards for acceptable urine-mercury concentrations. The American Conference of Governmental Industrial Hygienists (1990) has indicated plans to develop a biological exposure index (BEI) for mercury, (2) but has not yet done so. In British Columbia, the Workers' Compensation Board has published criteria for urine-mercury concentrations in mercury-exposed workers. Urine-mercury concentrations of less than 250 micrograms mercury per litre of urine (250 μg/L) are acceptable in this jurisdiction. (3) Health and Welfare Canada (4) used 50 μg/L as the maximum acceptable urine-mercury concentration when assessing worker urine concentrations.

Asbestos insulation in the Wheelhouse and boat deck was more than 95% amosite; the remainder was crocidolite asbestos. The target air concentration for cleanroom, adjacent occupied areas, and for final clearance sampling was 0.05 fibres per cubic centimetre of air (0.05 f/cc). Exposed metal surfaces were not spray sealed with encapsulant as is normally done following asbestos removal because of the recognized need for further cleaning in order to achieve further mercury decontamination.

The disposal of mercury contaminated waste is not permitted when mercury concentrations exceed 100 parts per million (ppm). Since asbestos wastes were likely to contain more than this concentration of mercury, all contaminant was stored, double bagged, in 45-gallon steel drums for further analysis and disposition.

The British Columbia Worker's Compensation Board (3) and Labour Canada do not permit uncontrolled mercury exposures at greater than 0.05 mg/m^3 airborne concentration. This concentration was exceeded in the Wheelhouse prior to decontamination and was likely to be exceeded during mercury decontamination procedures and during site preparation for asbestos removal. Workers carrying out each of these tasks wore half-face respirators fitted with mercury vapour cartridges. These cartridges provided effective protection for concentrations up to 0.5 mg/m^3. Air monitoring was provided using direct-read mercury monitors to ensure that higher mercury concentrations were not encountered.

For protection from both asbestos and mercury vapour during asbestos removal work, workers were required to wear full-face respirators fitted with compressed breathing air supply. The air supply was located on the aft section of the boat deck. The supplied air source was monitored hourly to ensure that mercury contaminant was not present in the compressed breathing air.

During asbestos removal, hourly monitoring of mercury vapour concentrations in the adjacent occupied areas, clean room, shower, and negative air exhaust outlets (3) was done. All results were recorded and reviewed. Mercury monitoring was done using a Jerome Model 411 Gold-film Mercury Monitor.

Work Program

The work program to decontaminate the ship was developed in four phases as follows:

1. Decontamination of equipment by the Ship's crew.
2. Asbestos removal by a private asbestos removal contractor.
3. Further decontamination of exposed metal surfaces by the Ship's crew.
4. Sealing uncleanable metal surfaces.

Briefly, mercury decontamination was done by a process of surface cleaning using a mercury decontaminant, HgX^R (Acton Associates, Pittston, Penn.). The process involves repeated washing with clean solutions of HgX^R to remove mercury contaminant until tests demonstrated acceptable concentrations of residual mercury.

The Ship's crew was instructed in the hazards of mercury, personal protective equipment use including gloves, coveralls and respirators, and prescribed work procedures. The crew cleaned equipment and supplies from the Wheelhouse and boat deck cabins. Once cleaned, this equipment was removed to storage. If decontamination was not possible, the equipment was packaged for disposal.

Decontamination by the Ship's crew then progressed to the cleaning of hallway, mess, galley and room walls, ceilings and floors. The tile on the boat deck hallway was removed for disposal due to extensive contamination between and under loose tiles. The subfloor was cleaned and protected with polyethylene until completion of all decontamination work on the vessel.

During the selection of an asbestos removal contractor, the unusual nature of this work was discussed with a short list of contractors. The selected contractor was then provided with detailed indoctrination regarding mercury work requirement, worker training needs, and personal protective equipment requirements. The contractor was further instructed in the requirements for limited use of spray encapsulant on exposed metal surfaces, and the need for thorough washing and cleaning of all traces of residual asbestos from these surfaces instead.

Asbestos removal by the contractor was carried out in two phases involving first the Wheelhouse and then the boat deck cabins. Work procedures are summarized as follows:

- Construct decontamination facility.
- Dismantle Wheelhouse consols and move these away from bulkheads.
- Remove bulkhead wood strapping and deckhead panels exposing underlying asbestos and accumulated mercury.
- Consultant collects bulk quantities of mercury exposed at base of bulkheads using vacuum trap equipment.
- Package wood strapping and other non-asbestos wastes in bags for removal to 45-gallon drums.
- Remove friable asbestos insulation materials from bulkheads and deckhead of Wheelhouse, and from deckhead of boat deck cabins.
- Remove floor tile and underlying mastic from Wheelhouse floor/cabin floors.
- Fine clean all exposed surfaces to remove all traces of asbestos.
- Store all asbestos debris in 45-gallon drums.

Packaged wastes were randomly sampled to determine mercury content in bulk asbestos, wood and other wastes. In total, ten percent of the drums of waste were opened and the contents sampled. Mercury concentrations were calculated for each type of waste. The test drums were weighed. Based on the weight of test drums and percent mercury an estimate of the total amount of mercury in the combined waste was calculated.

Parallel and subsequent to the decontamination work, the risk of past and future exposure of members of the Ship's crew was assessed. Individual medical assessments and biological monitoring of each crew member was done. Because total decontamination of the Wheelhouse to acceptable standards of surface contamination could not be achieved, all metal surfaces were sealed. Subsequently, a one year program of air monitoring was undertaken using Jerome Mercury Dosimeters.

Results of Decontamination

The clean-up took seven weeks; the asbestos removal contractor was on-site for 19 days of this time. Mercury vapour monitoring was done throughout this period. A summary of mercury vapour concentrations measured during decontamination is given in Table 1 for each area of the vessel.

Table 1

Summary of Mercury
Vapour Concentrations

Period	**Location**	**Range of Mercury Concentration (mg/m^3)**
Before clean-up	Wheelhouse	0.026 - 0.160
	Boat Deck	0.000 - 0.074
	Main Deck	0.000 - 0.018
Cleaning and equipment removal	Wheelhouse	0.000 - 0.018
	Boat Deck	0.000 - 0.087
	Main Deck	0.000 - 0.028
Asbestos removal	Wheelhouse	0.020 - 0.821
	Boat Deck	0.010 - 0.010
Further mercury cleaning	Wheelhouse	0.000 - 0.314
	Boat Deck	0.000 - 0.027
Final Clearance	Wheelhouse	0.000
	Boat Deck	0.000
	Main Deck	0.000

Notes:

1. Breathing zone concentrations.
2. Test exhaust air of negative air unit during asbestos removal phase.
3. Main deck contains cabins, galley, and mess.

The risk of mercury exposure was most significant in the Wheelhouse and to a lesser extent on the boat deck. Half-face respirators with mercury vapour cartridges were used throughout this work except during asbestos removal when the contract workers used air-line respirators. Use of air-line respirators ensured protection from high concentrations of both asbestos and mercury. Mercury vapour concentrations of 0.00 - 0.425 mg/m^3 were measured during preparations for asbestos removal in the Wheelhouse and boat deck. The limit (0.5 mg/m^3) of the mercury vapour cartridge respirator used by all workers were not exceeded, but without constant (hourly) monitoring, use of these respirators would not have been acceptable. During this phase all asbestos was fully enclosed behind wall and ceiling panels, hence protection from asbestos was not required.

During asbestos removal work, exhaust air from the negative air units was tested to assess work area mercury vapour concentrations. Mercury vapour concentrations up to 0.812 mg/m^3 were recorded with a geometric mean daily maximum concentration of 0.381 mg/m^3. These concentrations of mercury were present throughout the asbestos removal phases despite the discharge of more than 4000 cubic feet per minute of air from the work area. To demonstrate the extent of mercury contamination, some handfuls of asbestos, when squeezed, released droplets of liquid mercury.

In comparison, measured occupational exposures to asbestos averaged 21.6 f/cc (0.46 to 74.4 f/cc). On only one occasion measuring 0.033 f/cc, did airborne cleanroom or background fibre concentrations exceed 0.02 f/cc.

In order to carry out this work, the contractor had to make several changes to the normal work practices used in asbestos removal. Most significantly, HEPA vacuum cleaners were not permitted in the contaminated work area since mercury contamination of motor windings would have resulted. These machines would become an ongoing source of mercury contamination since decontamination is not possible. Since negative air units did not cycle used exhaust air for cooling of the motors, these were of less concern. Even so, exhaust air was discharged through the negative air units only because the ship was berthed in an unoccupied area more than one-quarter mile from any residence or industry. Air monitoring at the perimeter of the dockyard demonstrated no detectable mercury. The contractor was required to dispose of all filters in the waste barrels.

The contractor was not permitted to seal the exposed metal surfaces with spray sealant since further cleaning to remove mercury was expected to be necessary. It was found that the mercury had penetrated not only into the asbestos but also into the porous surfaces of the structural metal. Despite substantial efforts, cleaning was impossible. Heat applied to the surfaces readily generated more airborne mercury. Trials demonstrated that epoxy paint could seal the mercury. As a result, the metal surfaces throughout the Wheelhouse were painted with several coats of epoxy paint.

Mercury contamination of the boat deck was much less severe. Metal surfaces were cleaned to an acceptable level. Contaminated suspended ceilings and floor surfaces were disposed of as mercury-contaminated waste.

The contamination of remaining surfaces on the boat deck and main deck was less than on the Wheelhouse surfaces (Table 2). The ceilings, walls, and floors in these areas were cleaned using decontaminant wash. It was necessary to remove floor tiles to permit cleaning below.

Table 2

Analysis of Waste for Mercury Content

Waste Material	Number of Samples	Mercury Content Range (μg/gm)	Average Mercury Content (μg/gm)
All materials	16	4.5 - 3420	413.6
Friable asbestos	6	68.5 - 3420	922.2
Wallboard and wood	5	13.1 - 104	34.0
Flooring materials	4	4.5 - 1610	434.3
Exhaust unit HEPA filter	1	---	33.0

Analysis of collected wastes demonstrated substantial mercury content. The results of mercury analysis are reported in Table 3. Asbestos materials analyzed for mercury content demonstrated an average of 922.2 μg mercury/Kg of waste. From the data in Table 3, it is calculated that 1.92 Kg of mercury remained mixed in the waste. This significant concentration of mercury had accumulated in the asbestos insulation and other components over approximately 28 years because of the evaporation-condensation cycle previously described.

Table 3

Assessment of Mercury Surface Contamination Swab Samples

Location	**Mercury Surface Concentration**					
	Before Cleaning (μg/m^2)			**After Cleaning (μg/m^2)**		
	Low	**High**	**Avg**	**Low**	**High**	**Avg**
Wheelhouse						
• Bulkheads before removal during ACM removal phase	437.5	825	631.25			
• Metal exposed by asbestos removal	70	375	210			
Boat Deck						
• Bulkheads	1.5	170	85.75	2.0	75	23.4
• Deckhead				1.75	30.0	12.9
Main Deck						
• Bulkheads	1.0	31.5	8.1	0.75	22.5	6.6
• Floors	65	550	349.5	7.0	85	26.5

Notes:

1. Boat deck cabins and hallway floor surfaces removed and replaced.
2. Main deck hallway floors removed and replaced.
3. $\mu g/m^2$ = micrograms per square metre of surface area.
4. Wheelhouse metal surfaces were coated in epoxy as a final control step.

The disposal to landfill of waste containing more than 100 micrograms mercury per gram (μg/gm) waste is not permitted in British Columbia. These regulations applied also to asbestos waste which under normal conditions would go to regulated landfill. The options available for discharge of the asbestos waste from this project were to store the material in a hazardous waste storage site or to ship it out of province for landfill disposal in a secure hazardous waste landfill site. Shipment of wastes to such a site in Idaho was selected.

On completion of the decontamination, a waste management contractor was selected to dispose of all waste materials from this project. Contained waste in the barrels (163) was found loosely packed with substantial void space. Barrel content weighed an average of 31.1 Kg (9.1 Kg to 54.8 Kg). None of the bags were reported to be broken open, however, there was substantial water in the bottom of some barrels due to leakage of bags. To meet the 90% fill criteria of the disposal site, repackaging for landfill involved opening each barrel and pouring absorbent around the three to four contained bags. By reorganization of the bags in barrels, the total number of barrels was reduced by 20% saving landfill, absorbent qand transportation costs. The above repackaging efforts were required in order to address the different criteria for disposal of mercury as compared to asbestos wastes. A major difference being that wet packaging of mercury and other hazardous wastes is not permitted as it is for asbestos which is destined for local landfill. By minimizing moisture content, the integrity of the barrels is maintained and the potential for leaching is reduced. The disposal contractor determined not to separate asbestos and other highly contaminated waste from wood which was less contaminated. Separation of waste streams by the asbestos contractor would have been the only efficient way of achieving this reduction in mercury-contaminated waste.

Results of Medical Monitoring

In the spring of 1989, a team of two medical specialists (Health and Welfare Canada) took a detailed medical history of all crew members. Emphasis was placed on neurological and renal systems. A complete blood count, SMA-12, urinalysis and urine protein tests were done, as well as phycological testing. The medical examination, as well as blood and urine tests, were reported as negative.

In February, April and September of 1989, morning urine samples from crew members were collected and analyzed for mercury content. The timing of these tests covers the period before clean-up, during clean-up, and four months after completion of the clean-up. The results are summarized in Table 4. In comparison with Health and Welfare Canada criteria for occupational exposure to mercury (50 μg/L) the measured urine mercury concentrations are low but significant. The highest individual test result was 42.5 μg/L. A distinction to be made, however, is the fact that the persons on the Ship did not consider themselves to be mercury workers. The presence of measurable mercury concentrations in all tested workers in March, 1989, demonstrates the extent of mercury spread through the vessel.

Table 4

Summary of Urine-Mercury Data

Test Date (1989)	March	April	September
Number of workers tested.	23	25	20
Mean Hg Concentration (μg/litre)	19.3	16.5	6.1
Standard direction (S.D.)	11.44	8.28	1.87

Note:

Using Student t-test analysis for small sample number, there is no significant difference between date for March or April, there is a significant reduction in urine-mercury concentrations between March and September, 1989.

By September 1989, all workers showed reductions in urine-mercury concentrations. The highest concentration measured was 11 μg/L. This can be compared to a normal maximum of 10 μg/L for an occupationally non-exposed population. (5) These data parallel the reduced airborne concentrations of mercury both at the end of the decontamination work and over the subsequent year. The half-life of mercury in men is reported to be approximately 40 days. (1)

Results of Follow-Up Air Testing

Following decontamination to the fullest extent possible, tests demonstrated the presence of imbedded mercury in the structural metal of the Wheelhouse. These surfaces could not be decontaminated. As a result, they were sealed with epoxy paint (three coats). To determine the long-term effectiveness of this action, monthly air monitoring tests were done in the Wheelhouse and boat deck over the following year to determine the potential for future mercury release from coated metal surfaces.

The data are summarized in Table 5 for the monthly dosimetry tests (8 or 12 hour samples located in fixed locations) and survey monitoring. Over the year, temperatures ranged from 17°C to 29.6°C in the test locations.

Table 5

Summary of Mercury Dosimetry

	Wheelhouse			Cabins	
	Port	Centre	Starboard	Captains	Engineers
High (mg/m^3)	0.006	0.008	0.004	0.006	0.002
Low (mg/m^3)	<0.001	<0.001	<0.001	<0.001	<0.001
Most recent reading	<0.001	<0.001	<0.001	<0.001	0.001

Notes:

1. Using Jerome Model 412 Dosimeters and desorption onto Jerome Model 411 Mercury Monitor.
2. During morning and afternoon surveys with the Jerome Model 411 monitor, site specific mercury concentrations up to 0.012 mg/m^3 were detected.
3. Duration of dosimetry sampling was dependent of length of time vessel sailed on the test date (8 hr or 12 hr shift).
4. Dosimeters were positioned in fixed locations, approximating the breathing height of a worker.

Mercury vapour concentrations are demonstrated to remain well within an acceptable range. From August 1989 through September 1990 daily mean concentrations above 0.001 mg/m^3 (8 hour or 12 hour average) were not detected. This is equal to the U.S. EPA National Emission Standard (6) for mercury. Spot tests with the survey instrument, demonstrated some localized mercury concentrations (0.002 - 0.012 mg/m^3) most often near heat sources (radiator) or where sunshine struck directly onto coated metal surfaces.

Discussion

Accumulated mercury on the floor of the Wheelhouse was spread by vaporization and deposition onto all surfaces. Further migration outside the Wheelhouse occurred by leakage through floor openings and by tracking on footwear. Exposure of the Ship's crew occurred through inhalation and ingestion.

Decontamination was successfully completed using a combination of surface cleaning, and removal of contaminated materials and products. The decontamination process is labour intensive, involving repeated washing with a mercury decontaminant containing sulphur-based chemicals and EDTA. Achieving surface contamination of less than 125 μg of Hg/m^2 controls vapour release. In areas other than the Wheelhouse, floors were the surfaces of greatest contamination. It is probable that tracking on footwear was the cause of this contamination.

Of importance is the recognition that over time, mercury can penetrate metal surfaces, especially if those surfaces are corroded from age and contact with salt water. Previously, penetration of mercury condensate into new mild steel was observed following vaporization in a fire. (7) It has been demonstrated during this work that subsequent mercury vaporization can be prevented by treatment of the metal surfaces with epoxy paint.

The effectiveness of the decontamination was demonstrated by reduced urine-mercury concentrations four months after completion of the clean-up and by air monitoring studies carried out over a further one-year period.

Asbestos removal is often considered an independent component of many renovations or demolition projects. In this situation, the asbestos removal had to be done with full awareness of other project components. The two major concerns were the expected need to provide further decontamination to remove residual mercury, and the different waste disposal criteria. The project was carried out in recognition of the first difference, but waste disposal options had been considered only to the point that local landfill would likely not be permitted and that waste containment would have to be secure. In future projects of this nature, separation of waste at the point of generation would be worthwhile to reduce the volume requiring regulated disposal.

Several hygiene aspects of the project required full contractor awareness and supervision of the additional personal protective equipment and decontamination needs. All of the above factors demonstrate critical differences in project management needs when asbestos removal is required in situations posing hazards beyond those familiar to the contractor or his workers.

When asbestos is contaminated with a serious occupational contaminant such as mercury, there is little option but to remove the source of the mercury, which includes the contaminated asbestos. The requirements of a successful removal project in these circumstances include a broad-based knowledge of occupational hygiene principles, as well as project management skills.

References

1. National Institute for Occupational Safety and Health: Criteria for a Recommended Standard - Occupational Exposure to Inorganic Mercury DHEW (NIOSH) Pub. NO. 73-11024, U.S. Government Printing Office, Washington, D.C. (1974).

2. American Conference of Governmental Industrial Hygienists, 1990-91 Threshold Limit Values and Biological Exposure Indices, ACGIH, Cincinnati, OH (1990).

3. Workers' Compensation Board of B.C., Health and Safety Regulation, WCB, Richmond, B.C. (1978).

4. Williams, H.R., Medical Officer, Public Health Service, Health and Welfare Canada, Ottawa, personal communication (June, 1989).

5. Friberg, L. and Vostal, J., eds: Mercury in the Environment, CRC Press, p. 112 (1972).

6. Environmental Protection Agency, Clean Air Act, Federal Registry 38: 112, p 8820 (6 April, 1973).

7. R. Lockhart, unpublished X-ray diffraction data.

A COMPARISON OF STEAM STRIPPING AND AIR STRIPPING FOR THE REMOVAL OF VOLATILE ORGANIC COMPOUNDS FROM WATER

by

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INTRODUCTION

For many years air stripping has been used to remove volatile organic compounds (VOCs) from water. Recently controversy has surrounded the use of air stripping because of the potential air pollution problem. Usually, the solution to this problem is to treat the off-gas from the air stripper with a carbon adsorption, but this method also causes concern, because the expense of incinerating or regenerating the carbon is relatively large. Landfilling of the carbon may not be as expensive, but in many areas contaminated carbon is considered a hazardous waste and, therefore, secure landfill space for this type of material is difficult to find.

In 1986, the Emergencies Engineering Division (EED) (formally the Environmental Emergencies Technology Division) began looking at alternative methods for VOC removal from water for use in emergency and contaminated site situations. Steam stripping was one of the technologies investigated. An initial study performed by CH2MHill Engineering Consultants of Calgary showed that steam stripping is a cost effective method for removing of VOCs from water (1). It also showed that some semi-volatile compounds (semi-VOCs) could be removed by steam stripping which could not be removed by air stripping.

Following this study, EED contracted CH2MHill to construct a mobile steam stripping unit. The unit was used for the first time during a demonstration at a contaminated site in Gloucester, Ontario, during the summer of 1990. Two air stripping designs have also been tested at this site. A general comparison can be performed based on the data obtained during the Gloucester trials.

AIR STRIPPING - THEORY AND DESIGN

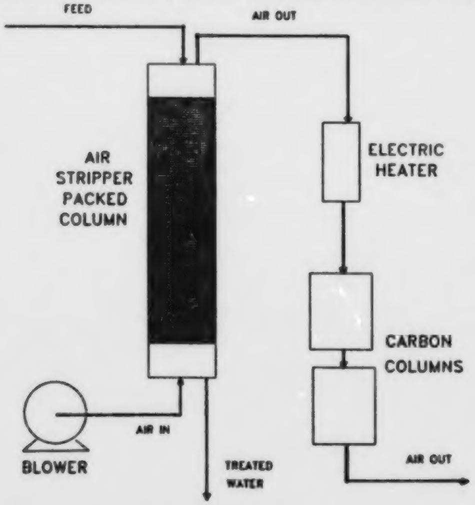
Generally, air stripping units allow air to come into contact with contaminated water causing the VOCs to transfer from the water to the air. The contact between the two phases is achieved by a variety of methods. Most traditional air stripping columns are counter-current packed columns. These systems have high mass transfer of VOCs, which results in high removal efficiencies. Several other air stripping designs exist, including cross-flow towers, multi-stage aerators and spray column air strippers (2).

At the Gloucester landfill two air stripping designs have been evaluated, a packed column air stripper and a multi-stage aerator. Both systems used carbon adsorption for off-gas treatment.

In 1986, the packed column was tested by members of Environment Wastewater Technology Centre (WTC) at this site (3). Figure 1 shows a schematic of this system. The air stripping column was 180cm high and 15cm in diameter. Both Intalox saddles and Rashing rings were evaluated as packing types. Packing diameters of 1.3cm and 1.9cm were tested for each packing type. In all cases the column diameter to packing diameter ratio was greater than eight. The feed stream entered the column at the top through a distribution nozzle while air entered through the bottom from an air blower.

The off-gas was treated through two activated carbon columns placed in series. The carbon used was Calgon's BPL type. Before being passed through the carbon columns the relative humidity of the off-gas was reduced by passing the gas through an electric heater.

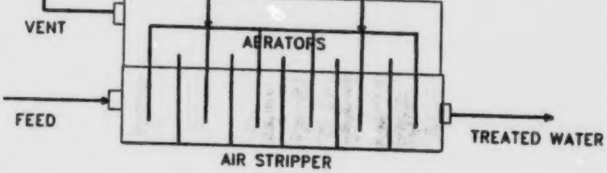
FIGURE 1: WTC AIR STRIPPING PACKED COLUMN SCHEMATIC (3)



In 1990, a multi-stage aerator was evaluated at the Gloucester landfill site. A schematic of the system used is shown in Figure 2. The system was provided by Lowry Engineering Inc. of Unity, Maine. This unit consisted of a 2.1m(L) by 0.7m(W) by 0.8m(H) high density polyethylene vessel with an airtight lid. The vessel was separated into six stages, each containing one aerator (4). As requested by the Ontario Ministry of Environment, a carbon adsorption unit was added to the air vent system, to treat the off-gases.

For low flow applications, the stage aerator has proven to be more cost effective than packed column designs, because a smaller unit is required to achieve a similar removal efficiency to a packed column. The packed tower is dependant on the air to water ratio and the packing height. For some compounds the required packing heights are very high and therefore two towers are frequently required. The stage aerator is dependant only on the air to water ratio so that, for difficult to remove compounds, there is not a requirement to increase the size of the unit.(4)

FIGURE 2: LOWRY MULTI-STAGE AERATOR SCHEMATIC (4)



STEAM STRIPPING - THEORY AND DESIGN

Steam stripping is based on the same concept as air stripping except that steam is used as a stripping medium to remove organic compounds from contaminated water. The steam containing the organic compounds can be condensed, resulting in a concentrated water stream instead of contaminants remaining in the gas phase, as with the air stripping process.

In the steam stripping process, the steam is fed into the bottom of the column while the feed stream enters into either the middle or the top of the column. The liquid feed stream comes into contact with the steam within the packing, causing volatile and some semi-volatile compounds to be transferred from the liquid to the vapour phase. This transfer is driven by the potential created by the concentration gradient between the liquid and vapour phases. The outlet vapour stream (tops) is condensed and sent to a decanter to separate any sufficiently concentrated organics from the aqueous stream. The treated liquid outlet (bottoms) can either be re-injected into the groundwater well or, if the outlet levels are above discharge limits, treated further. If the bottoms stream is very low in organics and de-ionized, it can be used to feed the boiler and therefore close the process cycle.

The system is set-up so that the aqueous phase from the decanter can be recycled back into the top of the column. If there is no phase change in the decanter then a specific percentage of the decanter inlet flow is refluxed. If the stream to be treated contains very volatile or low solubility contaminants then a reflux stream may not be needed.

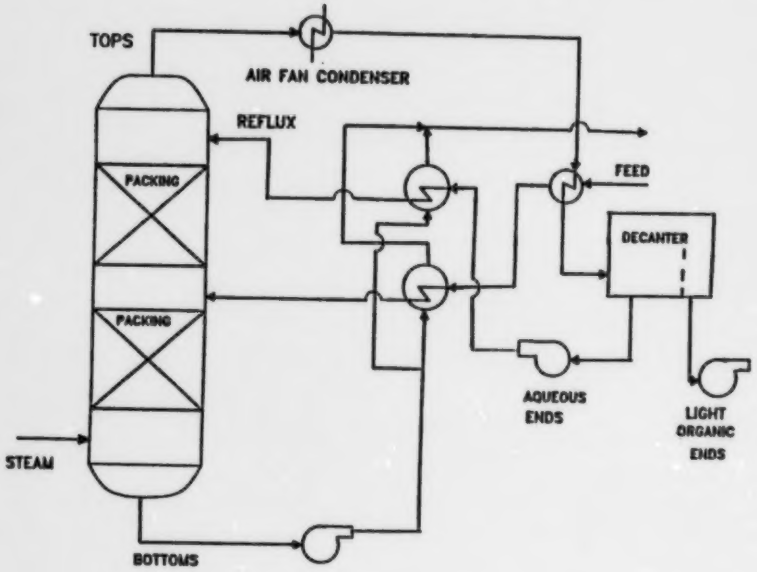
The EED steam stripping unit was built in 1987 by CH2MHill Engineering Limited in Calgary, after a feasibility study showed that steam stripping is an efficient process for removing volatile and semi-volatile organics from water. Its design is based on a typical industrial steam stripper, but the unit is fully mobile and can be disassembled to fit into an 18 foot cube van. The design specifications of the unit were based on the requirement that the unit be mobile and adaptable to remote areas and the Canadian climate. The ease of transport, set up and take down makes it ideal for emergency situations.

A detailed process flow diagram, of the EED system, is shown in Figure 3. This unit has a design feed rate of 2000L/h and a steam to feed ratio of up to 20%. The stripping section consists of a 0.31 diameter by 8.38m high column packed with 25.4mm diameter pall rings.

From the system diagram it can be seen that the heat transfer potentials have been used efficiently within the system. The feed and reflux streams are preheated by the purified liquid leaving the bottom of the column. The overhead, contaminant rich vapour, is initially condensed using an air cooled condenser. The stream is further cooled using the cold feed stream.

The system is fully enclosed, apart from a vent located on top of the decanter. This vent allows any vaporized volatiles in the decanter to travel through a small carbon column before entering the atmosphere.

FIGURE 3: EED STEAM STRIPPING SCHEMATIC (1)


TOPS
AIR FAN CONDENSER
REFLUX
PACKING
PACKING
FEED
DECANTER
AQUEOUS ENDS
LIGHT ORGANIC ENDS
STEAM
BOTTOMS

COMPARISON BETWEEN AIR STRIPPING AND STEAM STRIPPING

Both steam stripping and air stripping have distinct advantages and disadvantages as VOC treatment technologies. Steam stripping units generally have a higher capital cost than air stripping. As well, steam stripping can be costly to operate, because of the expense of producing the steam, but in many cases steam stripping will prove to be less expensive than the combination of air stripping and off-gas treatment.

Due to recent regulations it is required, in most areas, to have some form of off-gas treatment for air stripping systems. In the U.S., almost all states are initiating air toxicity programs, and because most VOCs are considered toxics, air strippers will be affected by these regulations. As well, the U.S. Superfund Amendment Reauthorization Act of 1986 (SARA) guidelines also require that the remediation of U.S. EPA superfund sites takes place without using technologies which transfer the contaminants from the water into the air. (5)

In most cases, the off-gas treatment used with air strippers is carbon adsorption. The addition of a carbon unit to an air stripping process greatly increases the treatment cost. The carbon either has to be landfilled as a hazardous waste, incinerated or regenerated. The regeneration usually involves thermal treatment or steam stripping. There is also added cost because, the relative humidity of the air must be reduced to less than 50% by a heating system in order for the carbon to effectively adsorb the contaminants in the air (5).

Carbon adsorption units must also be monitored closely because several compounds, such as 1,2-dichloroethane, readily desorb after being adsorbed on the carbon (6). As soon as breakthrough takes place the carbon column must be removed. For this reason, a backup carbon column is always required and a continuous monitoring program must be incorporated into the system.

Table 1 compares the various treatment aspects of air stripping, air stripping with off-gas treatment and steam stripping. The range of contaminant types which can be treated with steam stripping is much greater than with air stripping. Generally, compounds with Henry's law constants greater than 10^6 atm m^3/mol can be removed well with steam stripping, whereas for a compound to be removed by air stripping it must have a Henry's law constant greater than 10^3 atm m^3/mol (7). This indicates that there are several compounds which can be removed by steam stripping which cannot be removed by air stripping, including several alcohols, phenols, aldehydes and amines. Preliminary data show that the EED steam stripper is able to remove several of these compounds. Data from other steam stripping studies provide chlorinated phenol steam stripping removal efficiencies in the 75% - 99% range (1,8,9).

In an ideal mixture, steam stripping would not be able to remove compounds which have a lower volatility than water, but in actual fact many mixtures of dilute organic compounds in water form non-ideal mixtures which result in low boiling azeotropes. These azeotropes increase the relative volatility, making the compounds removable by steam stripping. Again, this phenomenon shows that steam stripping has the potential to remove far more compounds than air stripping.

Steam stripping will concentrate contaminants in the decanter and if the concentration is high enough (ie. above the solubility) the compounds will separate and can be decanted. In this form, the small volume of recovered contaminants can then be destroyed by other treatment methods at a low cost. If an individual component or a valuable combination of compounds are being removed, the compound(s) can be recovered for reuse.

TABLE 1: BASIC COMPARISON OF STEAM STRIPPING AND AIR STRIPPING

	AIR STRIPPING (PACKED COLUMN)	AIR STRIPPING WITH CARBON TREATMENT OF OFF-GAS	STEAM STRIPPING
RANGE OF TREATABLE CONTAMINANTS	VOCs Henry's law constant $>1x10^{-3}$ (atmm^3/mol)	VOCs Henry's law constants $>1x10^{-3}$ (atmm^3/mol)	VOCs and semiVOCs Henry's law constant $> 1x10^{-6}$ (atmm^3/mol)
STATE OF WASTE STREAM	air	spent carbon	contaminants concentrated in water

In general, steam stripping capital costs are greater than air stripping, because the stainless steel column required and the boiler, used to generate steam, are expensive. Air stripping with carbon off-gas treatment systems are relatively inexpensive, because many of the components are normally constructed from PVC.

Table 2 gives several examples of air stripping and steam stripping operating costs. These costs have been taken from various sources and in many cases the numbers have been converted to Canadian dollars and 1991 dollars. These costs could also vary greatly depending upon contaminant type and contaminant concentration. For these reasons the numbers can only be compared on a very general basis.

In comparing the increase in cost when carbon and carbon with regeneration is added to an air stripping unit it can be seen that the operating costs increase significantly. Using the costs presented in Table 2, the operating costs increases from 4 to 23 times when a carbon system is added and from 9 to 72 times when a carbon and a regenerating system are added. The estimated cost for regenerating carbon ranges from $\$0.48$ to $\$1.11/m^3$ (10). This range covers various regeneration methods, contaminant types and inlet concentrations.

Steam stripping unit operating costs are approximately 11 to 36 times greater than simple air stripping operating costs. However, when comparing steam stripping with air stripping plus carbon and carbon regeneration the costs are comparable for small units and the steam stripper costs are lower for the larger units.

There are also methods of lowering the costs of steam strippers even further by utilizing the latent heat resulting from the compression of the overhead vapour. Dow chemical has developed a system which adds "Mechanical Vapour Recompression" (MVR) to the system in order to transfer this heat to the production of steam for the system. Using actual case studies, Dow has quoted operating costs of $\$0.10\text{-}0.12/m^3$ for a $1090\text{-}1363m^3/d$ system using MVR (1991/cdn $).(8)

The higher steam stripping operating costs quoted in Table 2 are generally costs for treating some of the less volatile compounds, which require higher steam to feed ratio. Because this range covers compounds which are removable by steam stripping and not air stripping, care should be taken when comparing these higher costs with the air stripping costs.

TABLE 2: EXAMPLES OF STEAM STRIPPER AND AIR STRIPPER OPERATING COSTS

AIR STRIPPING ALONE (PACKED COLUMN)	AIR STRIPPING WITH CARBON OFF-GAS TREATMENT	AIR STRIPPING WITH CARBON OFF-GAS TREATMENT AND CARBON REGENERATION	STEAM STRIPPING WITH REFLUX AND RECTIFICATION SECTION
$\$0.02/m^3$ $1050m^3/d$ (3)	$\$0.33/m^3$ $1050m^3/d$ (3)	$\$0.81\text{-}1.44/m^3$ $1050m^3/d$ (3,10)	$\$0.22\text{-}0.26/m^3$ $1090\text{-}1363m^3/d$ (8)
$\$0.12\text{-}0.17/m^3$ $378m^3/d$ (12)[1]	$\$0.47\text{-}3.93/m^3$ $378m^3/d$ (12)[1]	$\$0.95\text{-}5.04/m^3$ $378m^3/d$ (10,12)[1]	$\$2.26\text{-}6.12/m^3$ $48m^3/d$ (1)

1. includes labour and maintenance costs

It is possible that, even with the addition of a method to destroy the compounds in the steam stripper's concentrated waste stream, the steam stripping operating costs would be comparable to air stripping with carbon regeneration. For example, a 48m^3/d steam stripping unit, such as the EED unit, run at a steam to feed ratio of 10% would produce 4.8m^3/d of concentrated waste. If the waste stream were to be destroyed using enhanced oxidation, the operating cost would only increase by $0.10 to $0.20/m^3 (11). This cost is based on the feed flowrate to the steam stripper and the enhanced oxidation costs for destroying VOCs, in the low ppm range, in water. Because the capital cost of an enhanced oxidation system can be very high, a full cost analysis must be performed in order to compare this process train with air stripping and off-gas treatment. As well, technology development has recently begun in the area of destruction of off-gas streams from air strippers using enhanced oxidation. This could also be a very cost effective system.

AIR STRIPPING GLOUCESTER RESULTS

During the 1986 Gloucester trial, the WTC packed column air stripper evaluation involved testing the two packing types, two packing sizes, two water flowrates (8L/min and 4L/min) and air to water ratios ranging from 15 to 110. (3)

The air stripping results from this trial showed that the range of removal efficiencies of the VOCs in the groundwater was 60% to 99.9%. The best removals were obtained using a 4L/min water flowrate, an air to water ratio of 110:1 and 1.3cm Rashing rings. The results using these conditions are presented in Table 3.

TABLE 3: PACKED TOWER AIR STRIPPER - GLOUCESTER 1986 BEST OBSERVED RESULTS (3)
feed rate = 4L/min Air:Water=110

COMPOUND	FEED (μg/L)	TREATED WATER (μg/L)	% REDUCTION IN CONC.
1,1 DICHLOROETHENE	13	0.2	98.5
TRICHLOROETHENE	17	0.2	98.8
1,1,1 TRICHLOROETHANE	41	0.1	99.8
TOLUENE	5	0.3	94.0
BENZENE	11	0.1	99.1
1,1 DICHLOROETHANE	34	0.3	99.1
CHLOROFORM	30	1.0	96.7
1,2 DICHLOROETHANE	76	4.0	94.7

During the multi-stage aerator evaluation, in 1990, the effect of altering the air to feed ratio was investigated (13). The feed was pre-treated using either a 0.21μm cross-flow microfiltration system or 5.0μm dead-end cartridge filters. The pH varied from 7.3 to 8.3. The feed was kept constant at 37.9L/min. The air supply was varied by varying the horsepower and number of blowers. The combinations ranged from using one 1HP blower to using three 2HP blowers. Throughout each run the back pressure from the system remained between 4.5 - 7.7 KPa.

The runs utilizing three 2HP blowers resulted in discharge concentrations below the remediation targets on all compounds of interest. Using fewer than 2HP blowers or using the 1HP blowers significantly reduced the concentrations of the VOCs but the required discharge limits were not reached for all compounds. Table 4 shows the results obtained using two 2HP blowers.

TABLE 4: MULTI-STAGE AERATOR - GLOUCESTER 1990 BEST OBSERVED RESULTS (13)
feed rate = 40L/min, 2 x 2hp blowers

COMPOUND	FEED (μg/L)	TREATED WATER (μg/L)	% REDUCTION IN CONC.
1,1 DICHLOROETHENE	395.0	14.7	96.3
TRICHLOROETHENE	511.0	0.17	>99.9
1,1,1 TRICHLOROETHANE	8013.0	0.95	>99.9
TOLUENE	4.11	0.3	92.8
BENZENE	388.0	1.58	99.6
CHLOROBENZENE	10.4	ND	>99.9
CHLOROFORM	255.0	0.84	99.7
1,2 DICHLOROETHANE	102.0	3.52	96.6
TETRAHYDROFURAN	149.0	7.85	94.7

STEAM STRIPPING GLOUCESTER RESULTS

In 1990, the EED steam stripping unit was also set up at the Gloucester landfill (13). Because this was the first time the unit had been set up and run on contaminated water, the main purpose of this trial was to examine the longterm effectiveness of the unit and to work out any of the preliminary equipment problems. The unit was run for approximately 23 hours with runs lasting from one hour to five hours. A total of ten runs were performed. The variables altered included the position of the feed inlet, whether or not the tops were refluxed and the times in which the samples were taken.

As with the air stripper, the feed to the steam stripper was pretreated using pH adjustment in conjunction with either 5.0μm filters or 0.2μm microfiltration. In order to provide the boiler with clean softened feed water, the bottoms stream from the steam stripper was passed through a mobile reverse osmosis unit.

Throughout the runs the feed flowrate remained between 30 and 33L/min. The volume ratios of steam to feed and waste steam to feed both varied between 10 to 15%. Because of the low concentrations of the contaminants in the water there was no phase separation present in the decanter.

In general, all VOCs, except trichloroethene, showed the greatest reduction in concentration when the concentrate stream was refluxed, regardless of whether the feed stream is fed midway or at the top. Benzene generally showed the greatest concentration reduction, followed by toluene.

In most cases the concentrations of the compounds in the bottoms stream were below the gas chromatograph detection limits and the remediation targets set by Ontario Ministry of the Environment. The only cases where compounds were over the remediation targets were runs without reflux.

The best results were obtained with the steam stripper when the feed was fed midway and the waste stream was refluxed. Using these operating conditions the steam stripper was able to reduce the concentration of all VOCs analyzed, to greater than 99.9%. This case is shown in Table 5. The percent reduction in concentration, in this table, is calculated from the feed and waste stream concentrations because almost all of the treated water streams were below the detection limits.

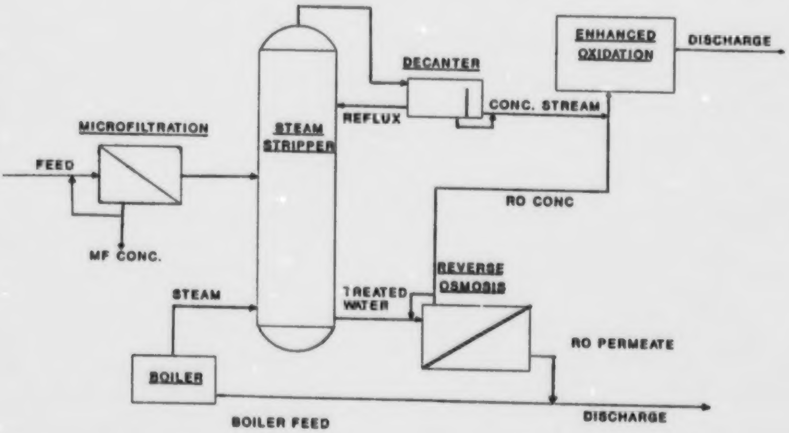
TABLE 5: STEAM STRIPPER - GLOUCESTER 1990 RESULTS (13)
feed rate = 33.3L/min steam/feed = 7/100

	FEED (ug/L)	WASTE STREAM (ug/L)	% REDUCTION IN CONCENTRATION
TRICHLOROETHENE	2800	65060	>99.9
TOLUENE	0.83	305.3	>99.9
BENZENE	1.78	12060	>99.9
CHLOROBENZENE	31.7	3205	>99.9
CHLOROFORM	157.8	4501	>99.9
1,2 DICHLOROETHANE	24.0	1104	>99.9
TETRAHYDROFURAN	836.9	18750	>99.9
ETHER	76.2	2342	>99.9

With a dilute feed stream, such as the Gloucester water, refluxing is required to further increase the concentration inthe waste stream. It is therefore not surprizing that the best results were obtained with reflux and a midway feed. Feeding midway allows the waste stream to be further concentrated in the top part of the column and the feed to be stripped in the bottom part of the column.

The highly concentrated waste stream resulting from the steam stripping process was passed through an enhanced oxidation unit which was able to destroy the contaminants to below discharge limits. It was shown that the combination of the enhanced oxidation unit and the steam stripper had the potential to completely remove and destroy the contaminants in the groundwater. Figure 4 provides a schematic of the process train used at the Gloucester landfill.

FIGURE 4: STEAM STRIPPER PROCESS TRAIN AT GLOUCESTER


ENHANCED OXIDATION
DISCHARGE
DECANTER
CONC. STREAM
REFLUX
MICROFILTRATION
STEAM STRIPPER
FEED
RO CONC
MF CONC.
REVERSE OSMOSIS
STEAM
TREATED WATER
RO PERMEATE
BOILER
BOILER FEED
DISCHARGE

LABORATORY ANALYSIS

The samples for both air stripping evaluations and the steam stripping evaluation were analyzed by gas chromatography. The steam stripping results were analyzed in EED's lab using a Hewlett Packard 5830 gas chromatograph (G.C.) with a 7675 purge and trap and a flame ionization detector. The 1990 air stripping samples were analyzed by a Hewlett Packard 5890 G.C. with direct headspace injection (model HP 19395A) and both an electron capture detector and a flame ionization detector. The 1986 air stripping samples were analyzed using purge and trap and flame ionization detection. (3,13)

DISCUSSION OF GLOUCESTER RESULTS

In comparing the results from the air stripping and the steam stripping runs presented above, it can be seen that in all cases the technologies were able to significantly reduce the concentration of the VOCs found in the groundwater. All the compounds shown have relative volatilities within the known removal range for both steam stripping and air stripping, so it is not surprising that both air stripping and steam stripping were able to remove these compounds.

In comparing the best observed results for each technology it can be seen that the steam stripper was able in reduce the concentration of all compounds listed to greater than 99.9%. The concentration reduction for the air stripping runs shown, ranged from 94.0 to 99.8% for the packed column and 92.8% to greater than 99.9% for the multi-stage aerator.

CONCLUSIONS

Both air stripping and steam stripping are effective technologies for removing volatile organic compounds from water. In comparing the operating costs of the two basic technologies, air stripping is considerably less expensive, but recent concerns over the air pollution created by air stripping have resulted in the need to add off-gas treatment. The addition of off-gas treatment, usually carbon with a regeneration system, increases the cost of air stripping substantially, making steam stripping a competitive technology. However, the advancement in new destruction methods for off-gas treatment may increase the favourability of air stripping for VOC removal. When comparing operating and capital costs, it must be kept in mind that steam stripping is a more flexible technology, because it is capable of removing a much wider range of compounds than air stripping.

A full comparison of the technologies should be performed on a case by case basis, because the capital and operating costs will vary with contaminant concentration and contaminant type. It is also recommended that for any VOC or semi-VOC remediation, a series of treatment techniques should be considered to increase the cost effectiveness and the decrease the need for off-site treatment of waste streams.

REFERENCES

1. CH2MHill Engineering Limited; Steam Stripping as an Emergency Countermeasure; Environment Canada Environmental Emergencies Report - EE91; November 1987; Ottawa, Ontario.

2. Kavanaugh, M.C. and Trussell, R.R.; "Design of Aeration Towers to Strip Volatile Contaminants from Drinking Water"; Research and Technology Journal of AWWA; December 1980.

3. Simovic, L.; "The Use of Air Stripping and Vapour Phase Adsorption Processes for the Removal of Volatile Organics from Contaminated Groundwater"; Environment Canada in-house publication WTC-PC-12-1988.

4. Lowry Engineering Inc; "Design and Application Guide for the Stripper Multi-staged Aeration Products"; 1990.

5. Cheuvront, D.A. et al; "Groundwater Treatment with Zero Air Emissions"; Environmental Progress; Volume 9; No. 3; August 1990.

6. Whittaker, H.; "Decontamination of Leachate and Groundwater at Chemical Landfills"; in Proceedings of the Symposium - Reclamation of Contaminated Soil - Technology; Economy and Law; Istituto per L'Ambiente Milan, Italy; January 1991.

7. Punt, M. et al; "Butane and Steam Stripping as Environmental Emergencies Countermeasures"; Proceedings of the 2nd International Conference on Separations Sciences and Technology-Vol.2; Hamilton, Ontario; October 1989.

8. Soloman, R.L. and Peterson, D.J.; "An Innovative Solution for Steam Stripping of Volatile Organic Compounds and High Boiling Point Pollutants from Groundwater with the AquaDetox Stripping System"; Proceedings of the 48th International Water Conference IWC-87-30; 1987.

9. Hwang, S.T. and Fahrenthold, P.; "Treatability of Organic Priority Pollutants by Steam Stripping"; AIChE Symposium Series; Water 1979; Volume 76; No. 197; 1980.

10. Fang, C.S. and Khor, S.; "Reduction of Volatile Organic Compounds in Aqueous Solutions Through Air Stripping and Gas-Phase Carbon Adsorption"; Environmental Progress Volume 8; No. 4; November 1989.

11. Clark, R.M. and Adams, J.Q.; "Evaluation of BAT for VOCs in Drinking Water"; Journal of Environmental Engineering; Volume 117; No. 2 March/April 1991.

12.L.M. Keller, Project Engineer; Emergencies Engineering Division, Environment Canada - personal communications.

13.L.M. Keller et al; "Comparative Evaluation of Groundwater Treatment Technologies at the Gloucester Landfill - 1990"; Environment Canada Report in Preparation.

RECENT APPLICATIONS OF ENVIRONMENT CANADA'S MOBILE ENHANCED OXIDATION UNIT

by

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ABSTRACT

The Emergencies Engineering Division (EED) of Environment Canada has investigated Advanced Oxidation Processes (AOP's) as a possible technology for chemical spill clean-up. The similarity between spill solutions and chemical landfill leachate, (and in some cases industrial streams), has enabled EED to conduct feasibility studies of this technology and collect a database of information for use at spill sites. This report briefly describes the technology and provides an overview of several pilot scale studies which were carried out using EED's mobile Enhanced Oxidation unit between 1989 and 1990.

BACKGROUND

EED has a mandate to evaluate and demonstrate new and existing technologies for the clean-up of chemical spills. Most of the technologies studied are in the form of mobile systems, which can be considered as alternatives to the conventional treatment techniques frequently applied to contaminated groundwater and industrial waste streams. As regulations on environmental protection emerge and standards (The Canadian Environmental Protection Act, CEPA) are set to manage toxic substances, government agencies are encouraging treatment technologies which meet both water and air emission discharge limits. CEPA became law on June 30, 1988 and focuses directly on pollution problems on land, in water, oceans and through all layers of the atmosphere. This new legislation gives the federal government broad powers to define national standards for any substance that threatens to harm the health and/or environment of Canada and its citizens.(Jacob, 1990)

AOP's are a family of related reaction processes that result in the oxidation of organic compounds. They are quickly becoming recognized as feasible, environmentally acceptable treatment technologies for destroying harmful organic compounds in water. These technologies have been developed to the point where they have become; in many cases, more technically viable, reliable and economical than the more traditional technologies such as carbon adsorption, air stripping and biological activated sludge, which have been shown to:

1) Be selective in their treatment of organic compounds;

2) Transfer contaminants from one medium to another and/or;

3) Require secondary disposal of contaminants (Gossett, 1990).

The oxidation of organic pollutants in water is an attractive method of treatment due to its ability to convert the compound to innocuous materials, such as carbon dioxide and water when carried to completion. If not carried to completion; however, partial oxidation usually results in products with enhanced biodegradability (Carey, 1990), an example being chlorinated hydrocarbons.

INTRODUCTION

The most common full-scale, commercially applied, enhanced oxidation processes, at this time, are those which involve the generation of the most highly oxidized species available; the hydroxyl radical (OH), as an intermediate product (Gossett, 1990). This very powerful oxidizing agent reacts very rapidly with virtually all organic compounds; and therefore, greatly increases the rate of oxidation when compared to traditional oxidation processes involving oxidants such as molecular ozone, hydrogen peroxide or hypochlorite. The rate of attack by hydroxyl radicals is typically one million (10^6) to one billion (10^9) times faster than the corresponding attack with molecular ozone.(Cater et al. 1990) The reaction mechanisms and chain reactions leading to the generation of the $^{\cdot}OH$ radical from ozone, H_2O_2 and UV light has been described by several authors[5-8]. The three most common pathways are described by the following simplified chemical equations:

1) PHOTOLYSIS OF H_2O_2 WITH UV LIGHT

$$H_2O_2 + h\nu \longrightarrow \longrightarrow 2OH^{\cdot}$$

2) THE REACTION BETWEEN OZONE AND H_2O_2

$$2O_3 + H_2O_2 \longrightarrow \longrightarrow 2OH^{\cdot} + 3O_2$$

3) FENTON's EQUATION

$$Fe^{+2} + H_2O_2 \longrightarrow \longrightarrow OH^{\cdot} + Fe^{+3} + OH^{-}$$

The further reaction of the OH radical with the organic compounds in question is largely dependant on the rate constant for that reaction as listed in Table 1 (Glaze and Kang, 1990)

TABLE 1

RATE CONSTANTS FOR THE HYDROXYL RADICAL

COMPOUND, M	$k_{m,OH}$ $(10^{+9} m^{-1} s^{-1})$
BENZENE	7.8
HYDROPEROXIDE ION	7.5
VINYL CHLORIDE	7.1
CHLOROBENZENE	4.5
1-BUTANOL	4.2
TRICHLOROETHANE	4.0
NITROBENZENE	3.9
PYRIDINE	3.8
TOLUENE	3.0
TETRACHLOROETHENE	2.3
CARBONATE ION	0.39
DICHLOROMETHANE	0.058
BICARBONATE	0.0085
CHLOROFORM	~0.005
CARBON TETRACHLORIDE	NR

Table 1 demonstrates that hydroxyl radicals are not very reactive towards chlorinated methane compounds. In fact, saturated aliphatics in general are quite unreactive towards the hydroxyl radical. This table also displays evidence that the carbonate and bicarbonate ions act as scavengers of the hydroxyl. (Scavengers is a term used for reactions of substances with OH radicals that do not yield species that propagate the chain reaction.)

EED's MOBILE UNIT (FIGURES 1 & 2)

The unit was originally designed to fit into the back of a 16ft cube van while having a maximum a treatment flowthrough capacity of 2000 L/hr.

The system is equipped with three vertical cylindrical stainless steel reactors, each containing a 6kW high power lamp, a quartz sleeve and a transmittance controller to prevent the sleeve from fouling. Injector systems for hydrogen peroxide (H_2O_2), ozone (O_3), pH adjustment and proprietary solutions are connected to the unit just prior to series of reactors. The unit has an air actuated system which is automatically or manually controlled by the operator from a schematic control panel. The flexibility of this system allows the operator to easily modify system parameters as required for system optimization. The high intensity proprietary lamps with output in the 195 to 300 nm range, enable virtually all organics to be destroyed. The creation of additional destruction pathways besides the hydroxyl radical attack, provides destruction mechanisms for even refractory compounds such as carbon tetrachloride, trichloroethane, or chloroform. The broad band of light source provided by these lamps, is emitted across the spectral region below 300 nm (Cater et al., 1990).

PERFORMANCE AND COST

There are numerous process variables which must be considered for each contaminated waste stream requiring treatment. Each parameter greatly affects the performance and cost effectiveness of the entire process. The main areas of consideration are listed below:

1) The nature of the contaminant - affects the choice of oxidant and catalysts; as well as, the type of UV light required.

2) The initial concentration - affects the amount of oxidant and catalyst required; as well as, the processing time.

3) The flow rate -affects the number, size and design of the reactors; as well as, the lamp power to be used

4) The degree of removal required - affects the processing time, the number and nature of the treatment stages; as well as, the reactor design.

FIGURE 1: PROCESS FLOW DIAGRAM

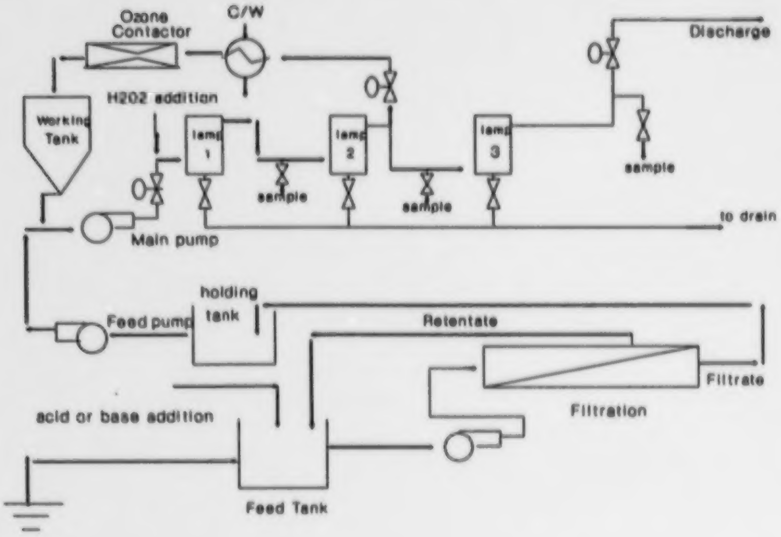
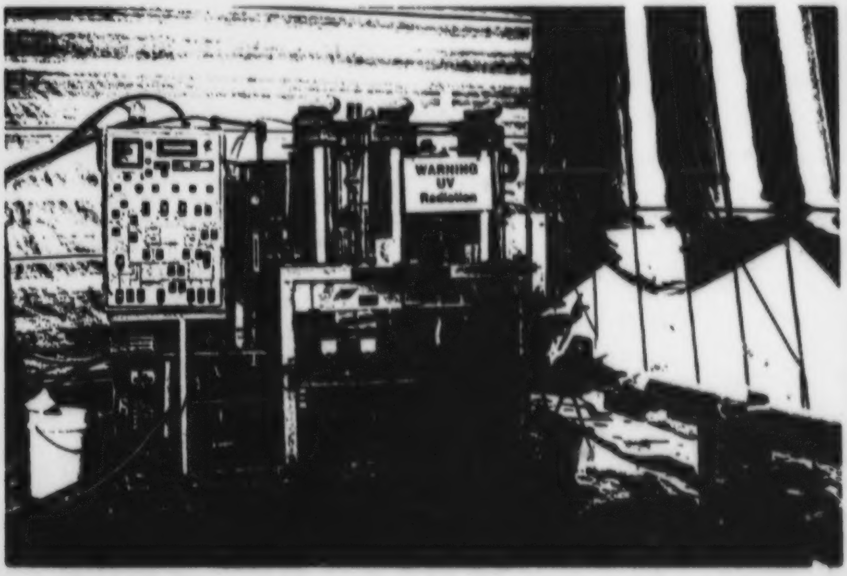

Ozone Contactor
C/W
Discharge
H2O2 addition
Working Tank
lamp 1
lamp 2
lamp 3
sample
sample
sample
to drain
Main pump
holding tank
Feed pump
Retentate
Filtrate
Filtration
acid or base addition
Feed Tank

FIGURE 2: EED'S MOBILE ENHANCED OXIDATION UNIT


WARNING
UV
Radiation

CASE STUDIES

The following sections of the report describe several pilot scale treatability studies carried out by EED's mobile unit between 1989-1990. Due to the confidential nature of the case studies, several site locations and company names have been omitted.

CASE STUDY 1

This study involved a six week trial to demonstrate the use of enhanced oxidation for the treatment of groundwater and an industrial waste stream contaminated with 1,4 dioxane at a concentration ranging between 20 and 110ppm.

The objectives of the study were as follows:

1) To confirm previous laboratory treatability study data for reducing dioxane concentrations in the groundwater

2) To evaluate both the UV/Ozone and UV/peroxide based treatment options for treating both raw and de-ionized water with each option.

3) To show that this technology was capable of destroying dioxane reliably and consistently.

4) To reduce the dioxane concentration to less than 3ppm for sewer discharge during a 24 hour pump test.

The groundwater feed to the unit was pumped both directly (raw) and via a deionization unit which removed iron and dissolved inorganic matter prior to destruction. In continuous mode the unit was operated between 19 and 114 L/min (5 and 30gpm). During the test period, operating conditions were varied until the system was optimized. Various test configurations were examined. They involved the use of UV, Enox 450[1], ozone, and Enox 510[1] in batch and continuous mode of operation.

---

[1] Enox 450 is a hydrogen peroxide based additive
Enox 510 is a water soluble rate enhancing additive which leaves no harmful residue.

RESULTS

Pump Test - Figure 3 illustrates the results achieved in the 24-hr pump test where the unit, operated at 75 L/min (20USgpm), reduced the dioxane level to below the target 2ppm. The three higher points were a result of the optimization process used during the tests.

Raw versus de-ionized water - The presence of iron and other dissolved inorganic matter in the raw feed resulted in lower destruction of the Dioxane in one of the wells, Figure 4. These compounds absorb some of the UV light, thus inhibiting the photolysis of peroxide to produce hydroxyl radicals as well as providing competition for dioxane in the reaction with hydroxyl radicals.

Enox 510 - Figure 5 provides a comparison of two runs with and without the rate enhancing additive (Enox 510). Since the treatment objective was 0.3ppm, the small benefit was not sufficient to justify it's use.

Ozone - Unlike the non-ozone based treatment, efficiency of dioxane destruction in deionized water did not improve over that obtained with the raw water. This is displayed in Figure 6.

OTHER FINDINGS

1) The system was able to reduce dioxane in either raw or de-ionized water consistently from 100ppm to <10ppb.

2) UV/PEROXIDE based system was a viable alternative to the ozone system with considerably lower capital costs and somewhat higher operating cost.

RECOMMENDED UNIT

A UV/H_2O_2 configuration provided the best performance /cost ratio. The recommended system was designed to treat the raw feed at 760 L/min (200USgpm) from 50 to 0.3ppm and higher concentrations at lower flow. This unit was preferred over the ozone configuration. Although the ozone system of the same design had a slightly lower operating cost, the capital cost was higher and off-gases (ozone or possible VOCs) would have to be treated prior to discharge.

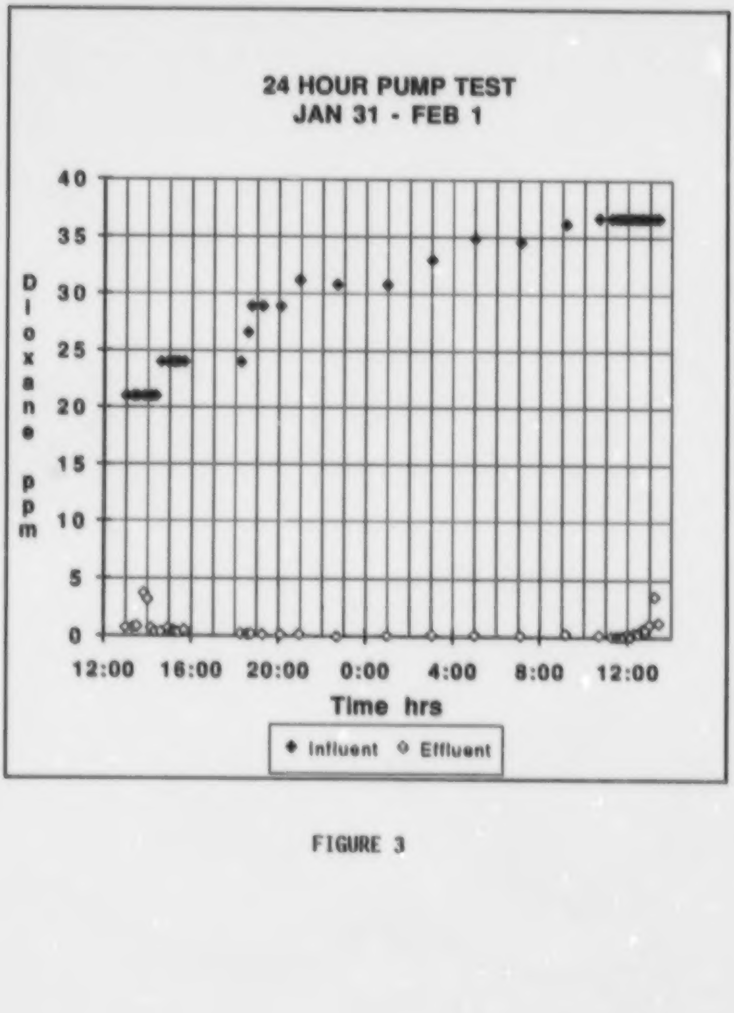

24 HOUR PUMP TEST
JAN 31 - FEB 1
Dioxane ppm
0
5
10
15
20
25
30
35
40
12:00
16:00
20:00
0:00
4:00
8:00
12:00
Time hrs
Influent
Effluent

FIGURE 3

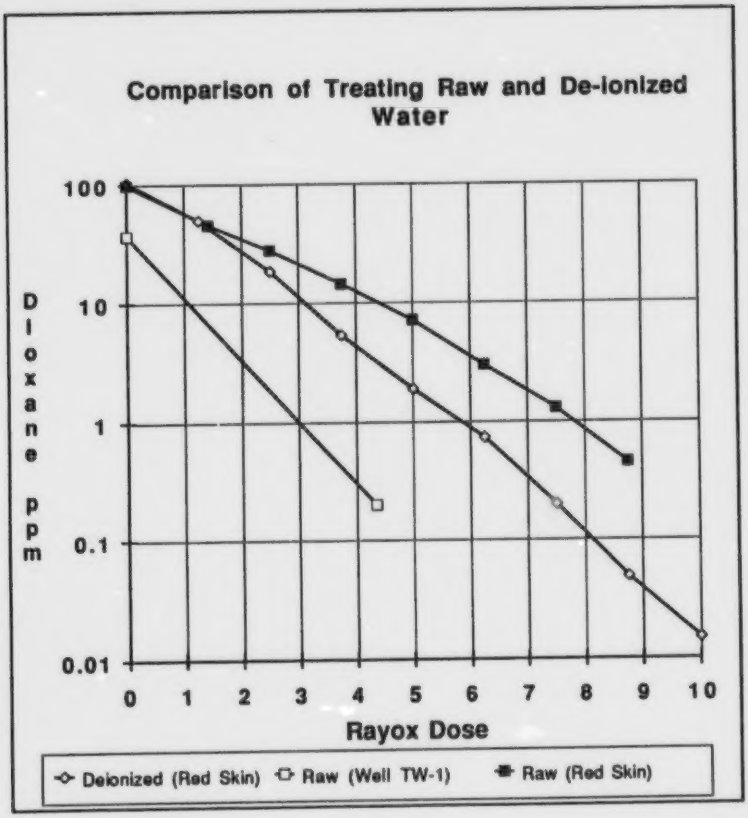

Comparison of Treating Raw and De-ionized Water
Dioxane ppm
100
10
1
0.1
0.01
0
1
2
3
4
5
6
7
8
9
10
Rayox Dose
Deionized (Red Skin)
Raw (Well TW-1)
Raw (Red Skin)

FIGURE 4

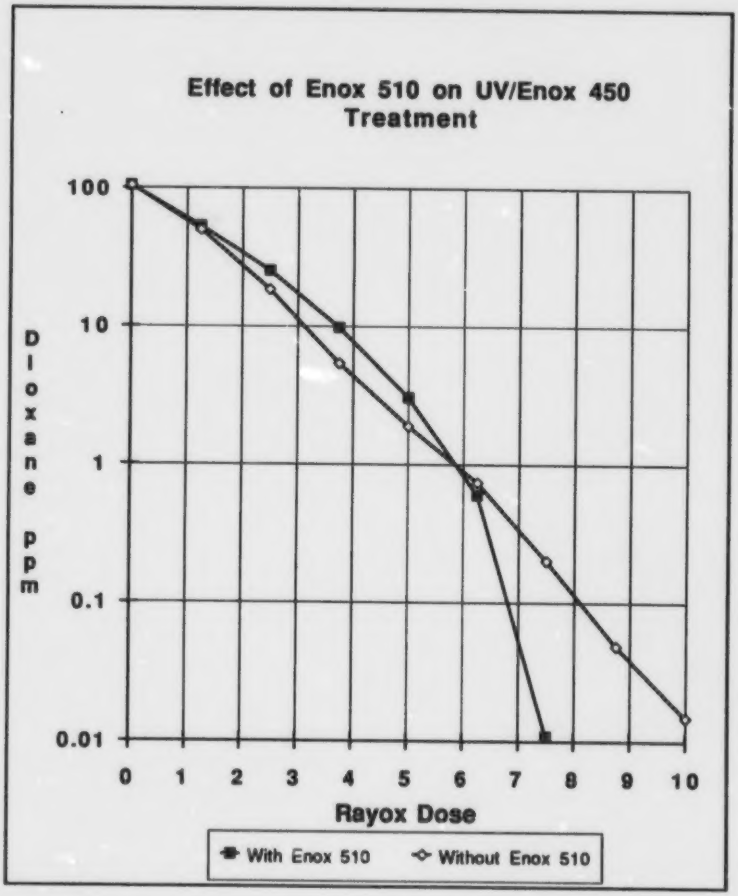
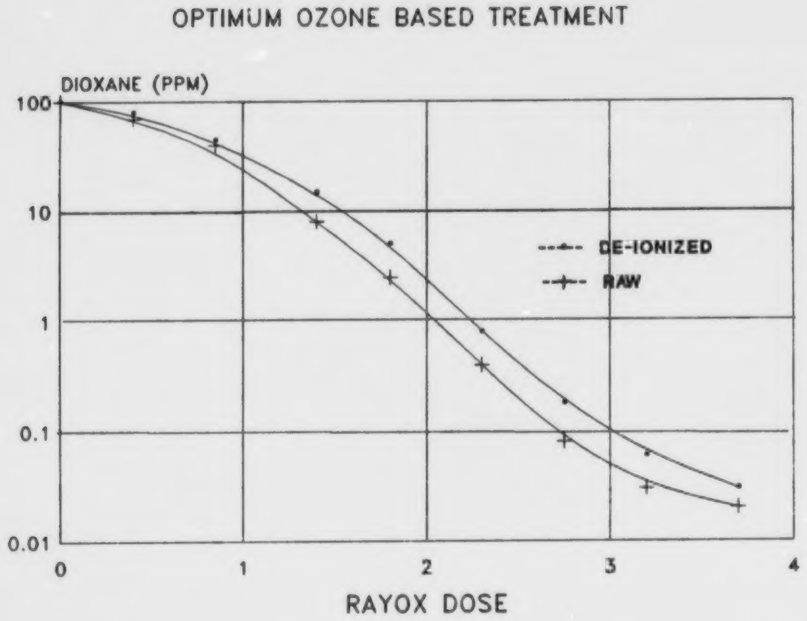

Effect of Enox 510 on UV/Enox 450 Treatment
Dioxane ppm
100
10
1
0.1
0.01
0
1
2
3
4
5
6
7
8
9
10
Rayox Dose
With Enox 510
Without Enox 510

FIGURE 5



OPTIMUM OZONE BASED TREATMENT

FIGURE 6

CASE STUDY 2

Another six week trial was carried out in February 1990 to investigate the feasibility of enhanced oxidation technology of the treatment on industrial wells contaminated with medium to high ppb concentrations of chlorinated aliphatic hydrocarbons.

The main objective of this trial was to determine the most cost effective approach to reducing the VOC concentrations to less than 5ppb at a flowrate of 23 L/min (6USgpm).
The VOCs of concern and their average feed concentrations were as follows:

COMPOUND	CONCENTRATION (ppb)
methylene chloride (MeCl,CH_2Cl_2)	130-730
trichloroethylene (TCE, $CHCl=CCl_2$)	9700-19900
1,2 trans-dichloroethylene (DCE, $C_2H_4Cl_2$)	6000-12500
vinyl chloride (VC, $H_2C=CHCl$)	10-1010
chloroethane (EtCl, C_2H_5Cl)	10

The testing was conducted in continuous mode of operation in all cases. A steady flow through rate of 20 L/min (5USgpm) was maintained during the trial period. As described in the first case study, process parameters were varied during the testing; however, high iron concentrations and the nature of the contaminant affected several of the system parameters. By maintaining a constant pH of 3, the precipitation of iron was prevented and the system was optimized. Ozone was not included as a test parameter due to the volatile nature of the components. Air stripping of the VOCs in an ozone /air stream would have simply transferred the contaminant from one medium to another, without destroying it.

RESULTS

A discharge level of <5 ppb for total VOCs was achieved with the mobile unit at a continuous flow rate of 19 L/min. The individual effluent concentrations of each compound are as follows:

COMPOUND	EFFLUENT (ppb)
MeCl	3.1
TCE	0.4
DCE	<0.1
VC	0.5
EtCl	<0.3

RECOMMENDED UNIT

A 40 L/min UV/H_2O_2 system operated at a pH of 3 was recommended for this groundwater stream. A baffled holding tank, with a residence time of approximately 20 minutes, was also included in the final design.

CASE STUDY 3

The third demonstration took place during the months of May and June of 1990. This 6-week trial involved the treatment of a variety of nitrate esters (explosives) in three wastewater streams.

The main objective of this trial was to determine the most cost effective approach to reducing the concentrations of each of the compounds to <1ppm. The five compounds of interest and their influent concentrations are listed in Table 2.

TABLE 2
INFLUENT CONCENTRATIONS OF EXPLOSIVE COMPOUNDS IN CASE STUDY 3

COMPOUND	SITE 1 INFLUENT CONC. (PPM)	SITE 2 INFLUENT CONC. (PPM)	SITE 3 INFLUENT CONC. (PPM)
NG	952-1009	N/A	1186-1212
TEGDN	N/A	3566-4630	N/A
TMETN	N/A	113-252	N/A
PGDN	N/A	N/A	277-2064

SITE 1

Five runs were conducted on this water stream with various UV/H_2O_2 doses; as well as, three runs with UV alone. The pH was maintained at a neutral level and the flowrates were averaged at 15 lpm (4 USGpm).

SITE 2

Five waste streams were treated at this site. All streams of both TEGDN and TMETN, contained high concentrations of carbonates (scavengers of the hydroxyl radical), except one. Previous bench-scale studies had shown that the carbonate could be precipitated with the use of lime. In this on-site study; however, the lime was not effective. Although UV photolysis successfully treated this stream, a more cost efficient design was investigated. This alternative involved proprietary pretreatment system to remove the carbonate without the use of lime. During removal of carbonate opens up a second channel of destruction when UV/peroxide is used, because the hydroxyl radical mechanism can also be used concurrent with straight UV photolysis.

SITE 3

At this site, the two composite streams containing separate compounds, both contained the UV blocking carbonates and nitrates, while the two recycle streams did not. As a result, the studies were separated. The runs on the composite streams involved four different treatment processed methods. A straight UV photolysis run proved effective, but uneconomical. The proprietary pretreatment/ UV/peroxide system, similar to the one studied in site 2, destroyed the compounds, but because the stream contained a higher concentration of UV blocking nitrates, it also proved to be very costly. Three runs were completed using the combination of lime/ozone, which was the recommended system from the previous treatability study. As before, lime was used to remove the carbonate as limestone precipitate. This sludge was left in the water, which had a milky colour, until after treatment PGDN to less than 1 ppm. Thereafter, the sludge can be separated as a non-hazardous waste. These runs also involved the recycling of unused ozone from the main reaction tank into a second tank, where it could be used further.

A total of six runs were completed on the two recycle streams. A run using straight ozone was unsuccessful, while straight UV photolysis provided the required destruction at a more economical cost than with the composite streams. The runs involving the use of both UV and hydrogen peroxide, proved to be successful; as well as, more economical than the straight photolysis.

RESULTS

The discharge objective of <1 ppm was achievable with all streams tested. Figures 7-13 present the graphical results of the three site studies at their optimum operating conditions.

RECOMMENDED UNIT

Table 3 summarizes the recommended systems and states whether or not scavengers were present in the various streams.

TABLE 3
RECOMMENDED SYSTEMS FOR CASE STUDY 3

SITE	STREAM	RECOMMENDED SYSTEM	SCAVENGERS	pH
1-NG	----	UV/H_2O_2	NO	7
2-TEGND, TNETN	composite	Proprietary pretreat./ UV/H_2O_2	YES	3
	recycle	UV/H_2O_2	NO	7
3-PGDN	composite	lime/ozone	YES	7
	recycle	UV/H_2O_2	NO	7

OTHER CASE STUDIES

Table 4 briefly summarizes several other case studies which have been carried out using EED's mobile unit. More detailed information on each of these sites is available through EED or Solarchem Environmental Systems.

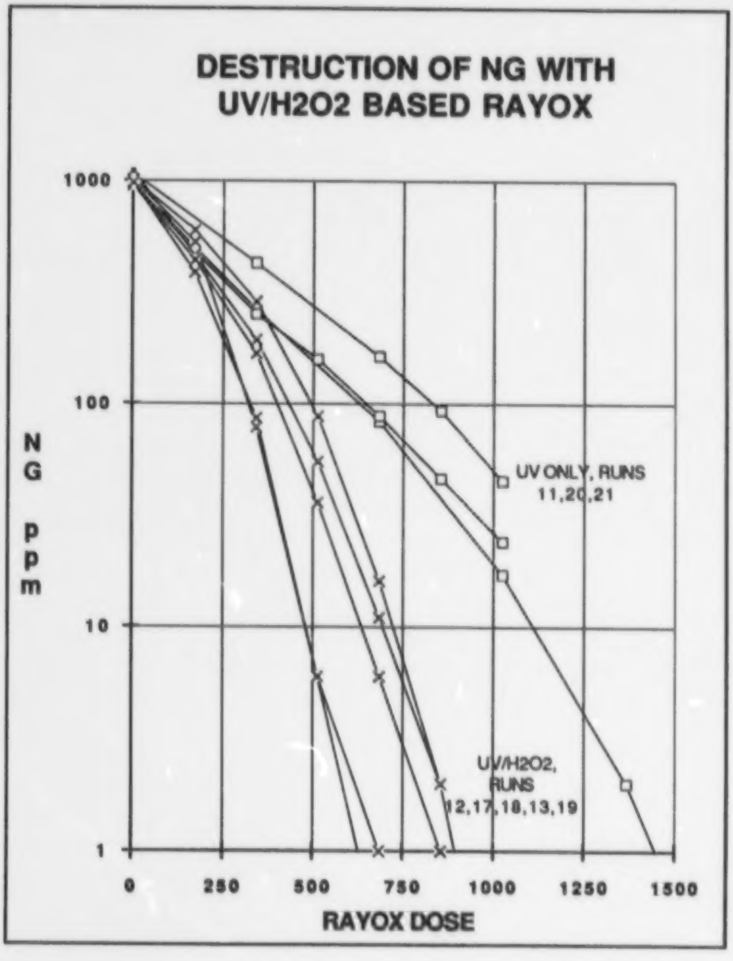

DESTRUCTION OF NG WITH
UV/H2O2 BASED RAYOX
1000
100
10
1
N G ppm
UV ONLY, RUNS
11,20,21
UV/H2O2,
RUNS
12,17,18,13,19
0
250
500
750
1000
1250
1500
RAYOX DOSE

FIGURE 7

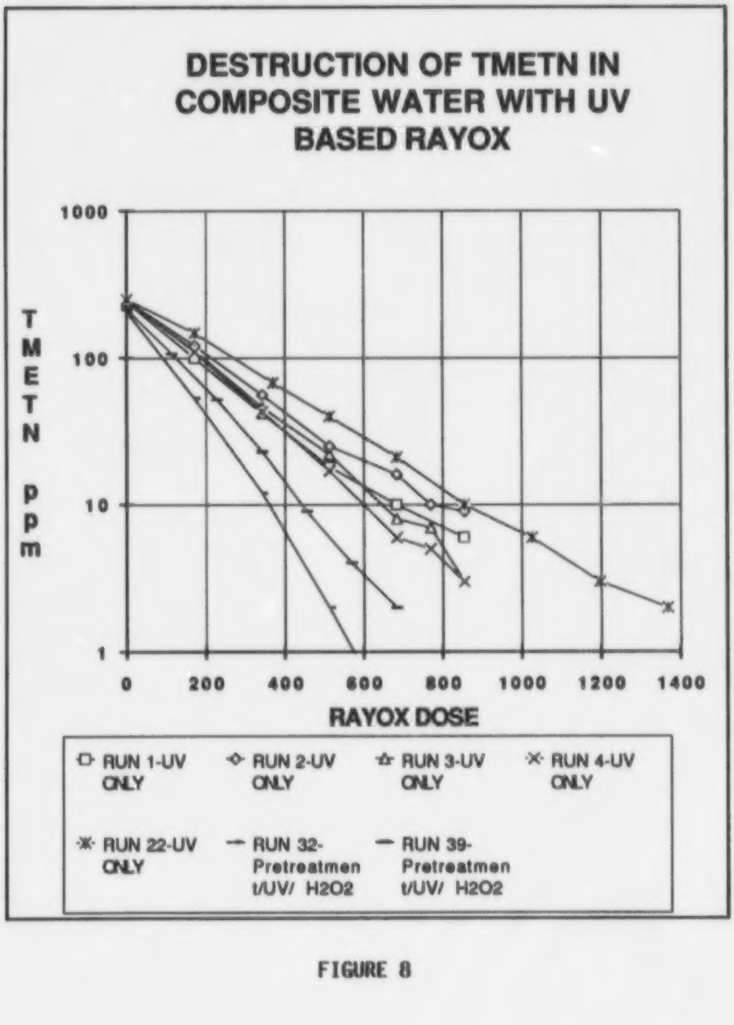

DESTRUCTION OF TMETN IN COMPOSITE WATER WITH UV BASED RAYOX
TMETN ppm
1000
100
10
1
0
200
400
600
800
1000
1200
1400
RAYOX DOSE
RUN 1-UV ONLY
RUN 2-UV ONLY
RUN 3-UV ONLY
RUN 4-UV ONLY
RUN 22-UV ONLY
RUN 32-Pretreatment/UV/ H2O2
RUN 39-Pretreatment/UV/ H2O2

FIGURE 8

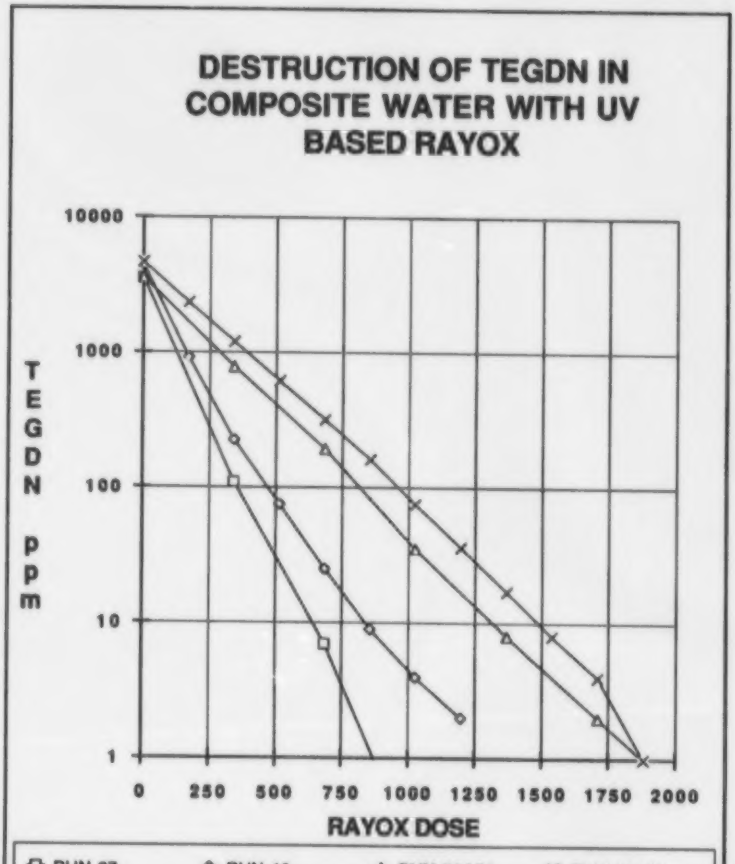

DESTRUCTION OF TEGDN IN COMPOSITE WATER WITH UV BASED RAYOX
TEGDN ppm
10000
1000
100
10
1
0
250
500
750
1000
1250
1500
1750
2000
RAYOX DOSE
RUN 37-Pretreatment/UV/H2O2
RUN 49-Pretreatment/UV/H2O2
RUN 36-UV ONLY
RUN 46-UV ONLY

FIGURE 9

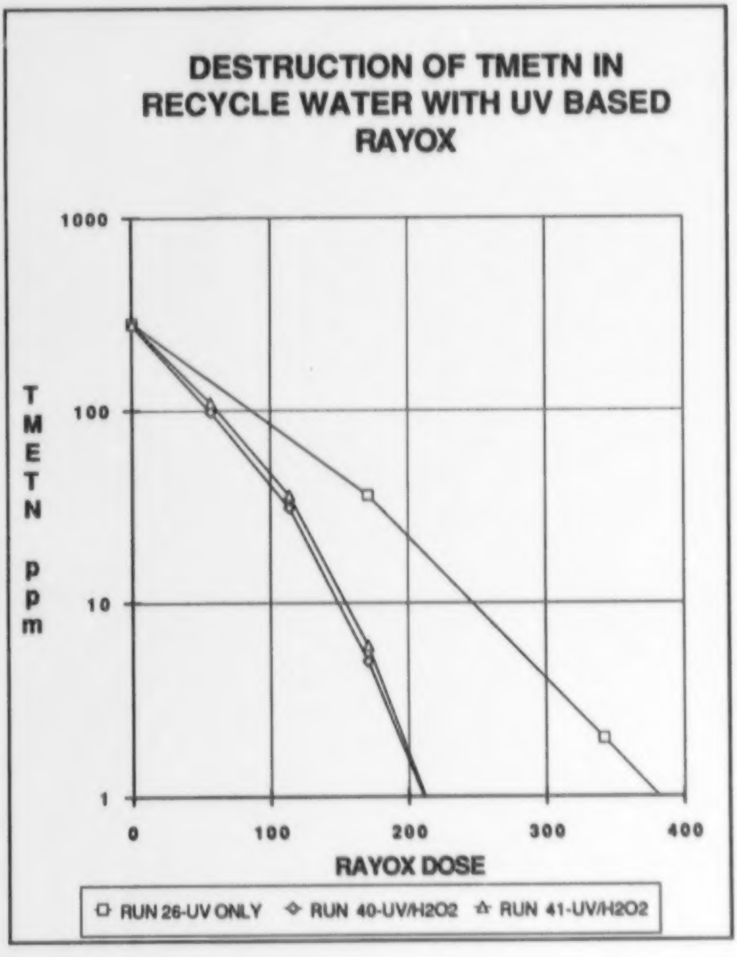

DESTRUCTION OF TMETN IN RECYCLE WATER WITH UV BASED RAYOX
1000
100
10
1
TMETN ppm
0
100
200
300
400
RAYOX DOSE
RUN 26-UV ONLY
RUN 40-UV/H2O2
RUN 41-UV/H2O2

FIGURE 10

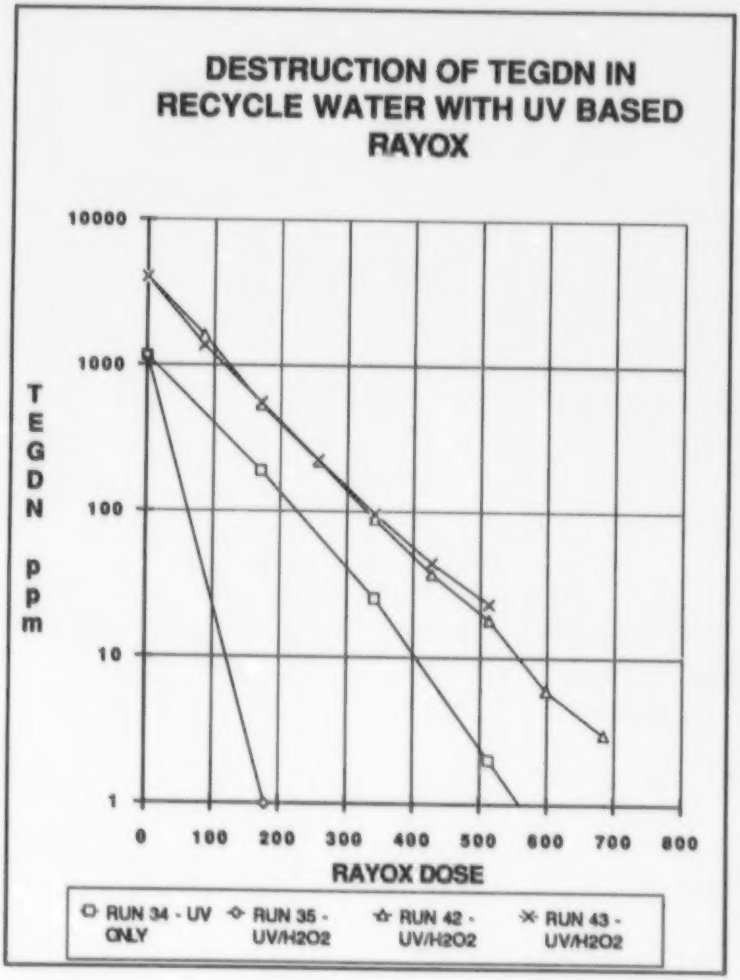

DESTRUCTION OF TEGDN IN RECYCLE WATER WITH UV BASED RAYOX
TEGDN ppm
10000
1000
100
10
1
0
100
200
300
400
500
600
700
800
RAYOX DOSE
RUN 34 - UV ONLY
RUN 35 - UV/H2O2
RUN 42 - UV/H2O2
RUN 43 - UV/H2O2

FIGURE 11

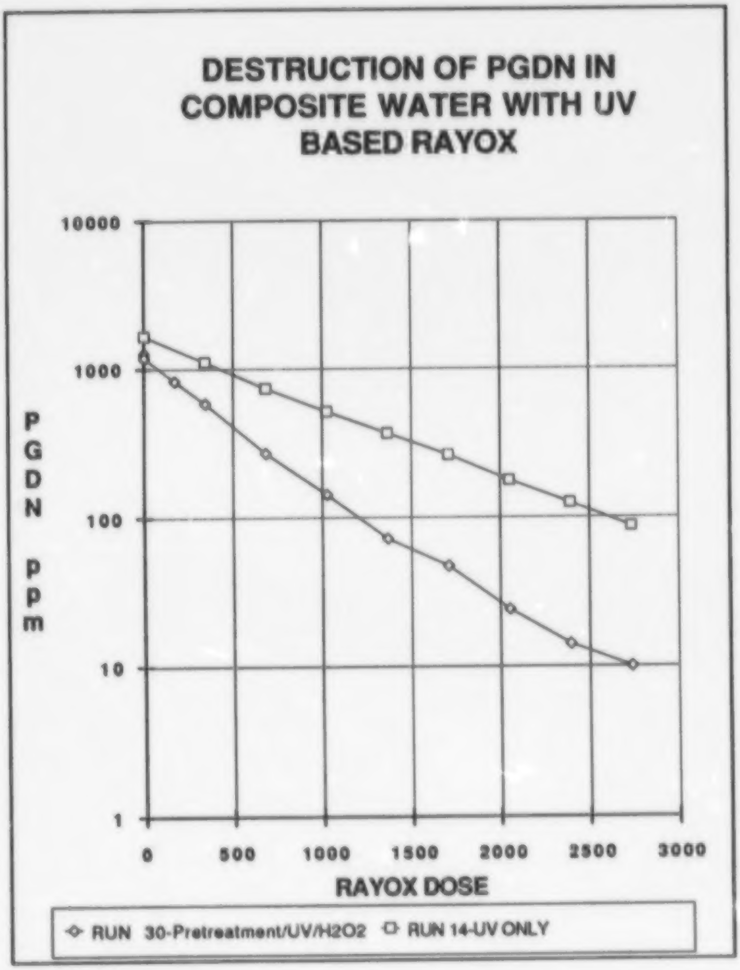

DESTRUCTION OF PGDN IN COMPOSITE WATER WITH UV BASED RAYOX
10000
1000
100
10
1
PGDN ppm
0
500
1000
1500
2000
2500
3000
RAYOX DOSE
RUN 30-Pretreatment/UV/H2O2
RUN 14-UV ONLY

FIGURE 12

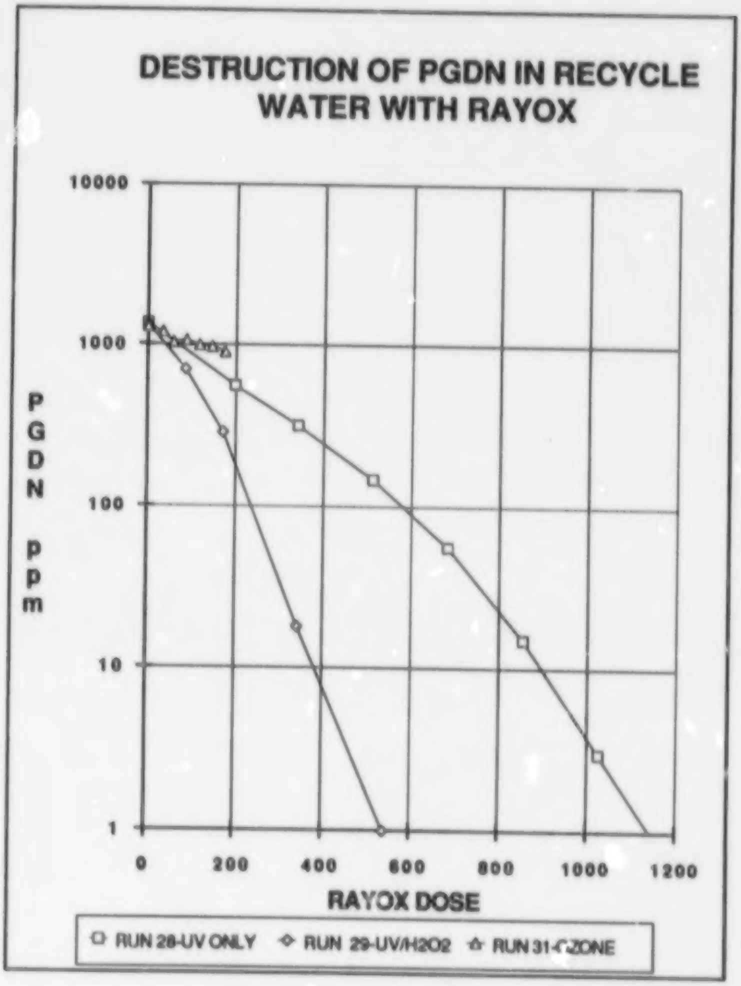

DESTRUCTION OF PGDN IN RECYCLE WATER WITH RAYOX
10000
1000
100
10
1
PGDN ppm
0
200
400
600
800
1000
1200
RAYOX DOSE
RUN 28-UV ONLY
RUN 29-UV/H2O2
RUN 31-OZONE

FIGURE 13

TABLE 4

OTHER CASES INVESTIGATED WITH ENHANCED OXIDATION

LOCATION	COMPOUNDS	INFL. CONC. (PPM)	EFFL. CONC. (PPM)	RECOMM'D SYSTEM
GLOUCESTER ONTARIO GROUND-WATER	TCE BENZENE CHLOROFORM CHLOROBENZ 1,2 DCA	1.551 0.228 0.081 0.054 0.012	0.0 0.0 0.037 0.0 0.0	pH_2 adjust/ MF[2]/UV/H_2O_2
NEW BRUNSWICK GROUND-WATER	BENZENE TOLUENE XYLENE	36 54 28	0.63 0.03 ND	MF/RO UV/H_2O_2 (ON CONC.)
QUEBEC, INDUSTRIAL WASTE STREAM	CN^-	6	2	UV/H_2O_2
US SUPERFUND SITE	DCE DCA BENZENE	0.5 5 3	ND ND 0.009	UV/H_2O_2/ ENOX 510

CONCLUSIONS

The case studies described in this report have provided the reader with an overview of the numerous applications available with the enhanced (advanced) oxidation technology. The total destruction capability of this treatment technique provides an economically, and environmentally acceptable method for treating waste streams containing organics at concentrations below 1% . Since many waste streams require more than one technology for effective treatment, EED will continue to incorporate this technology into their process train of technologies for treatment of chemical spills.

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[2] MF/RO Refers to the two membrane technologies, MICROFILTRATION AND REVERSE OSMOSIS. These techniques are used to remove inorganic foulants and to concentrate organics in dilute waste streams prior to enhanced oxidation.

REFERENCES

1. Jacob, Gisele; The Canadian Environmental Protection Act and The Fisheries Act: The Regulatory Agenda; A Symposium on Advanced Oxidation Processes; June 4 & 5, 1990.

2. Peyton, Gary R.; A Comparison of Advanced Oxidation Processes; Aquatic Chemistry Section; Illinois State Water Survey; Champaign, Illinois; 1990.

3. Carey, J.H.; An Introduction To Advanced Oxidation Processes (AOP) For Destruction of organics in Wastewater; Lakes Research Branch; National Water Research Institute Canada Centre for Inland Waters; 1990.

4. Gossett, N. and R. Harries; Technology Evaluation: Advanced Oxidation Processes vs. Conventional Treatment Technologies For Aqueous Contaminants; CH_2MHill, Inc.; Bellevue, Washington, U.S.A.; 1990.

5. Hoine, J.and H. Bader; The Role of Hydroxyl Radical Reactions in Ozonation Process in Aqueous Solutions; Water Res. 10; pages 377-386; 1976.

6. Prengle, H.W.; C.G. Hewes; C.E. Mauk; Oxidation of Refractory Materials by Ozone with Ultraviolet Radiation; Proceedings of 2nd International Symposium on Ozone Technology; International Ozone Institute; pages 224-252; 1976.

7. Peyton G.R. and W.H. Glaze; Destruction of Pollutants with Ozone in Combination with Ultraviolet Radiation & Photolysis of Aqueous Ozone; Environmental Science Technology; Volume 22; pages 761-767; 1988.

8. Paillard, H.; R. Brunet, and M. Dore; Optimal Conditions for Applying an Ozone Hydrogen Peroxide Oxidizing System; Water Res 22, pages 91-103; 1988.

9. Keller, L. and M. Punt; Comparative Evaluation of Groundwater Treatment Technologies at the Gloucester Landfill; 1990.

10. Cater et al; RAYOX: A second Generation Enhanced Oxidation Process For Groundwater Remediation; Proceedings- A Symposium on Advanced Oxidation Processes; June 4 & 5, 1991.

11. Choryhanna, G. and C. Adams; Demonstration of Membrane Technology in Atlantic Canada (1989).

AN OVERVIEW OF THE ENVIRONMENTAL RESPONSE TEAM'S AIR SURVEILLANCE PROCEDURES AT EMERGENCY RESPONSE ACTIVITIES INVOLVING HIGHLY REACTIVE AND TOXIC MATERIALS

by

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Edison, N.J. 08837-3679

INTRODUCTION:

The U.S. Environmental Protection Agency's Environmental Response Team (ERT) was established in October 1978 to provide technical assistance to all branches of the EPA, as well as other Federal/State governmental agencies and foreign governments in the area of environmental emergencies, such as chemical releases and uncontrolled hazardous waste sites. As part of the role as a national response team for environmental emergencies, the ERT has had the opportunity to conduct air sampling and monitoring during various activities, ranging from tire fires to detonation/treatment of extremely toxic or reactive materials throughout the United States and foreign countries.

This paper will describe the Safety and Air Surveillance Section's (SASS) organization for responding to emergency air releases, and the air surveillance equipment and procedures used by ERT. In addition, the paper will conclude with case studies that demonstrate various emergency response activities including: the detonation of 1,4-dioxane drums in Cotton Plant, Arkansas; oil well burning in Kuwait City; the detonation of 49 high pressure cylinders with unknown contents in America Samoa; and the burning of Hurricane Hugo debris in St. Croix, V.I.

SAFETY AND AIR SURVEILLANCE SECTION:

To manage for effective response to the various air surveillance activities, the Section has categorized air response activities into three basic groups:

1. Emergency Air Responses
2. Occupational and Human Health Air Responses
3. Remedial Air Responses

While this paper will only address the emergency air responses, it is important to realize that, at any given point in time, an occupational and public health air response or remedial air response can be an emergency activity. Ideally, however, the occupational and public health air responses deal with potential human problems suspected of either being related to site air releases/conditions or nearby air releases. The ERT's indoor air activities also fall into this category. Remedial air responses are those response activities which involve crucial environmental surveys to determine the fate and movement of airborne contaminants at waste sites or underground storage tank areas. This type of response would also involve determining air emissions rates during pilot clean-up operations and long-term exposure modeling.

EMERGENCY AIR RESPONSES:

Typically, an emergency air response involves an accidental release, fire, and/or explosion. Since the requested information is needed at the time of the phone call, planning and responding to an emergency air response are very difficult. In order to be able to obtain specific information regarding the content of the plume, SASS has put together emergency air response kits. These kits are contained in a large fishing tackle box and include sufficient collecting media and spare sampling train parts to start initial air sampling activities. In addition to these kits, various real-time organic and aerosol monitors are kept on charge and response ready.

The difficult part of responding to an emergency air release is determining which compounds to sample for and the analytical protocol for the compounds. To say that something is not present in the plume means that one must look for that compound. For this reason, we have modified the flow rates and sampling time of National Institute for Occupational Safety and Health (NIOSH) Manual of Analytical Methods(1). In some cases, we have also modified the analytical protocols in order to obtain lower detection limits. The reason for using the NIOSH Methods is that they identify a collection media for many of the compounds found in various industrial work places, which means they may be present at an emergency air release. Table 1 shows representative classes of compounds, collection media, flow rate and sampling times that have been used at episodic air releases.

TABLE 1

CONTAMINANT	NIOSH METHOD	FLOW RATE	MEDIA	SAMPLE TIME
Aromatic/ Halogenated Hydrocarbons	1500/1501	1 l/m	Carbon	2-4 hrs
Inorganic Acids	7903	1 l/m	Silica	2-4 hrs
Alcohols	1402	.5 l/m	Carbon	2 hrs
Acetic Acid	1603	1 l/m	Carbon	2 hrs
Acetal-dehyde	2538	1 l/m	ORBO-25 XAD-2	2 hrs
Aliphatic Amines	2010	.5 l/m	Silica	2-4 hrs
Aromatic Amines	2002	1 l/m	Silica	2-4 hrs

In addition, SASS has developed a sampling/analytical method to look at many of the volatile organics present in fire plumes. Tenax/CMS is usually run for two hours at 30 cc/min. in conjunction with real-time organic analyzers and aerosol monitors.

The following summarizes the various types of monitoring and sampling equipment used during an emergency air response:

1. PHOTOIONIZATION DETECTORS (PID)

A hand-held PID measures airborne, ionizable gases and vapors by using Ultra Violet (UV) light. The common Ultraviolet sources available are 9.5, 10.0, 10.2 and 11.7 electron volts (eV). When a molecule of contaminant enters into the ionization chamber and absorbs a photon, the molecule will be ionized if the energy of the photon is greater than or equal to the ionization potential of the molecule. Since the ionization potential of the major components of pure air are higher than 12 eV, they will not be ionized by any ultraviolet lamp mentioned above(2). The ionization potentials for many compounds may be found in the NIOSH Pocket Guide to Chemical Hazards(3).

The hand-held PID is more useful when identifying the presence of Total Organic Compounds rather than identifying a specific compound within a plume. A major disadvantage of most hand-held PID's is operating them in cold weather (below 5°C). This is because the Ultraviolet light source has a tendency to fog up much like a part of eye glass would when operating below freezing.

2. COMBUSTIBLE GAS METER (CGM)

Combustible gas meters (CGM) are hand-held, battery operated continuous duty monitors which provide efficient and reliable methods to test for potentially explosive atmospheres. At a minimum, CGM's usually measure the Lower Explosive Limits (LEL) and Oxygen content.

This is a "go/no go" type of instrument, and it does have a few limitations. For example, the CGM sensor can be "poisoned" by organic lead compounds used in leaded gasoline, and silicone compounds found in hydraulic fluids. Also, carbon dioxide enriched atmospheres reduce the oxygen sensor life.

3. REAL-TIME AEROSOL MONITOR (RAM)

The hand-held RAM is a monitor which displays total particulates (i.e., dust, mists, and aerosols). The instrument used by ERT employs a pulse light emitting diode which generates a narrow band emission. The instrument is very useful in determining the presence of a plume when it is not visible.

Since the light emitting diode is temperature dependent, discretion must be used when operating this instrument outside normal room temperature. In addition, water droplets, humidity and pollen may cause erroneously high readings.

4. PERSONAL SAMPLING PUMP

The traditional industrial hygiene personal sampling pump with a flow rate range of 0.2 - 3 l/m is the "work horse" of the emergency air response kit. These units are versatile, rugged, and reliable. The ERT units are a pneumatic pumping system with rechargeable battery packs which are easily replaced. The pumps have programmable timers which permit them to be turned on and off automatically.

About the only draw backs to these pumps are the fact that they are not fire proof and the pump is limited to a back pressure of approximately 25 inches of water. If pumps are being run in high humidity or the collection tubes have been packed too tight, the pumps may stop functioning.

5. HIGH FLOW PUMPS

The high flow pumps are not to be confused with the traditional high volume ambient air monitoring pumps. The high flow pump has a flow rate of 2 - 20 l/m with a telescopic sampling mast for the sampling train. Because of its high volume, this pump is suitable for sampling low concentrations of airborne contaminants, as well as asbestos and particulate sampling. Because of its size and AC power requirement, this pump is not routinely used during an emergency air response.

CASE HISTORIES

A. Cotton Plant, Arkansas

The ERT was requested to assist EPA Region VI in determining how to dispose of 55 and 35 gallon drums of 1,4-dioxane that was stored for the past 20 years in an old cotton warehouse. The compound, an organic ether, can form organic peroxides if stored for long period of times. Also stored in the warehouse were other drums of chemicals which included flammable liquids, arsenic and cyanide based solids. In order to dispose of the dioxane, it had to be moved to a remote location. Therefore, the other material had to be removed first in case an explosion occurred when the dioxane is moved. Water containers were placed at strategic locations to insure that the movement of the other chemicals would not cause the drums of dioxane to be shaken. Also, an infrared temperature monitor was used to assist in determining the amount of dioxane in the drums. The air monitoring consisted of an PID organic vapor monitor, a RAM for particulate, and cyanide electrochemical detector.

B. Oil Well Fires in Kuwait

The ERT was part of EPA's interagency Air Assessment Team that was responsible for assessment of the effects that the 500 Iraqi-set oil well fires were having on the health and the environment. The ERT members were responsible for performing real-time air monitoring and sampling in the oil fields and in Kuwait City.

The real-time monitoring consisted of taking readings for H^2S, SO_2, volatile organics, oxygen, and total particulate. The air sampling consisted of collecting samples for the following parameters:

polycyclic aromatic hydrocarbons, metals, volatile organics, inorganic acids, H_2S, SO_2, formaldehyde, and carbon monoxide. The sampling and monitoring was conducted at the following locations: US Embassy, Kuwait City; Camp Freedom, Kuwait City; Dhahran, Saudi Arabia; US Embassy, Riyadh, Saudi Arabia; Port Shuaybah, Kuwait; Al Maqua Oil Field, Al Ahmadi Oil Field, Al Ahmadi Hospital, Al Burgan Oil Field, Al Wafra Oil Field, and Sabiriyah Oil Field in Kuwait.

The results from this sampling and monitoring indicated that the fires were emitting high levels of soot, and low levels of the other materials being monitored.

C. American Samoa

The ERT was requested by EPA Region IX to provide assistance concerning the disposal of 49 high pressure cylinders in American Samoa. The cylinders were given to a farmer in 1950 who used them as part of a pig sty fence. In 1989, one or more of the cylinders leaked, causing damage to the surrounding vegetation. A preliminary investigation indicated that a majority of the cylinders contained either acetylene or chlorine gas.

After an evaluation of disposal options, it was determined that the cylinders should be remotely detonated and vented to the atmosphere in a remote location. This was accomplished by placing explosive charges on the cylinders and detonating them in a pit.

The ERT was responsible for performing air monitoring during all phases of this project which included preliminary assessment, handling and transportation, health and safety, and final disposal assessment. The monitoring was performed using PID, indicator tubes, and electrochemical detectors for the following parameters: volatile organics, hydrogen chloride, chlorine, phosgene, and hydrogen cyanide.

D. Hurricane Hugo

The Island of St. Croix in the U.S. Virgin Islands was devastated during Hurricane Hugo. The damage was extensive and required the disposal of large amounts of debris which consisted of wood, furniture, metal structures, etc. Because St. Croix is a small island, the Army Corps of Engineers decided that the best procedure to dispose of the debris was to burn it.

The ERT was requested by EPA Region II to evaluate the effects of the burning of the debris piles. In order to determine what materials might be emitted, the ERT performed some real-time monitoring during the burns. The monitoring consisted of taking measurement for the following parameters: sulfur dioxide, hydrogen sulfide, chlorine, hydrogen chloride, phosgene, cyanide, total particulates, carbon monoxide, and volatile organics. The ERT recommended to the region that the piles first be segregated and only wood material be burned in small increments.

CONCLUSION

ERT routinely performs over 200 response activities per year of which approximately 50% involve some type of air surveillance activities. The SASS responds to approximately 20-40 toxic air releases per year with 5-10 of these activities being international in nature. The authors hope that this information has been both helpful and enjoyable.

REFERENCES

1. "NIOSH Manual of Analytical Methods", National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering, Cincinnati, OH, NIOSH Publication No. 84-100, February, 1984.

2. "Draft International Document on Guide to Portable Instruments for Assessing Airborne Pollutants Arising From Hazardous Wastes", Organization Internationale De Metrologie, Published by American Conference of Governmental Industrial Hygienists, 6500 Glenway Ave., Building D-7, Cincinnati, OH, ISBN:0-936712-75-9.

3. "NIOSH Pocket Guide to Chemical Hazards", U.S. Department of Health and Human Services, National Institute for Occupational Safety and Health, Cincinnati, OH, NIOSH Publication No. 90-117, June, 1990.

Determination of low level hydrophobic contamination in water systems. A practical approach.

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Introduction

It has been suggested that regulatory agencies should be able to ensure no toxins present after the clean up of a spill event are above detectable limits[1] or in a more practical approach are below the No Observable Effect Level (NOEL)[2,3]. This can be a very demanding requirement when it is applied to extremely toxic hydrophobic contaminants in water systems. Compounds of this nature have the potential to bioaccumulate and thus an observable effect can be noticed even when trace concentrations are present[3,4]. At the present time a laboratory using a GC/MSD-full scan or GC/FID has a working instrumental detection limit in the ng/ul (ppm) range while when using GC/ECD or GC/MSD-SIM this limit drops to the pg/ul (ppb) range. Given sufficient time and expertise, concentration factors of 10,000 (from 1 L to .1 ml) and 100,000 (from 10 L's to .1 ml) can be obtained. This lowers the detection limit for 1 L into the range of .1 ppb for GC/MSD-full scan and GC/FID to .1 ppt for GC/ECD and GC/MSD-SIM. For a 10 L sample this translates to 10 ppt for GC/MSD-full scan and GC/FID and to 10 ppq for GC/ECD and GC/MSD-SIM. In cases when these detection limits are not acceptable it becomes impractical to collect, transport, and process larger volumes of water as required by traditional methodologies. This discussion will explain the development of an automated system which can improve detection limits by collecting a larger sample, in duplicate in a form that is easier to process while at the same time being more difficult to contaminate. Furthermore, the development of an automated sampling system is the first step in the automation of on site trace analysis which not only will provide more reproducible results, but also shorter analysis time.

Preliminary Concepts

Resin Application

The isolation of hydrophobic compounds from water is normally accomplished by introducing an immiscible hydrophobic liquid or a solid into the water system. The nature of this should be such that it can form an energetically favourable association with the analyte relative to the analyte / water association so that the analyte will become quantitatively partitioned into or onto this substance. The hydrophobic substance used in the MARK II APS for hydrophobic pollutants is amberlite XAD-2, a porous bead shaped synthetic polystyrene based polymer with an effective surface area of ~330 m^2/g and an average pore diameter of 90 Ånstroms[5]. The large surface area of the beads and the weak nature of the analyte/resin association make it ideal for this application. The difficulties arising from the use of XAD-2 resin include 1) tedious labour intensive clean-up procedure, 2) cleaned resin must be kept under deionized water or methanol, 3) relatively low flow rates (3 x resin bed volume = ~ 100 mls/min), and particulate bound analytes can pass through resin.

The presence of particulate in water systems complicates both the collection of analytes and subsequent analysis. When solutes in a water system contact these particles some equilibrium will develop. This equilibrium relationship is difficult to model as some of the characteristics of these particles are not well understood and their concentration and nature is considerably dynamic. Moreso, the presence of particulate bound analytes can facilitate break-through of the XAD column, in addition, particulate can clog resin pores, and generally reduce the effective surface area of the resin. A solution to these problems is to remove the particulate from the water prior to the resin using a filtration system.

Analytical Filtration

Much of the work on the APS has centred on finding an analytical grade filter suitable for the removal of particulate from large volumes of turbid water, while at the same time providing an interference free substrate for the subsequent extraction of analytes form the particles. A series of product surveys have been performed and the materials tested to determine the most appropriate products available. The data obtained in these studies in the form of contract final reports have been presented to MOE[6,7], and are available from this organization or the authors. The most suitable commercially available filter was determined to be the Balston Q series Microfiber tube filter (available from Can-Am Instruments) based on chemical resistance and lack of interferences for the dioxins[a] under study. However, the capacity of these filters is not sufficient enough to permit the processing of more than 40 L samples, never-the-less, the lack of a more suitable filter made this inadequacy tolerable. The Balston are classified as either Q or H type based on the use of fluorocarbon based or inorganic based binders respectively. The Q type was selected based on its superior resistance to mechanical damage. It was determined that a high percentage of the analytes spiked into the system were collected by the filter system. This occurred even when analytes were spiked into distilled, deionized water indicating that the analytes are selectively bound to the filter material. The use of filters as both a particle remover and an analytical substrate is discussed in a paper to be published in the near future[8] (see also tables 2,3,4).

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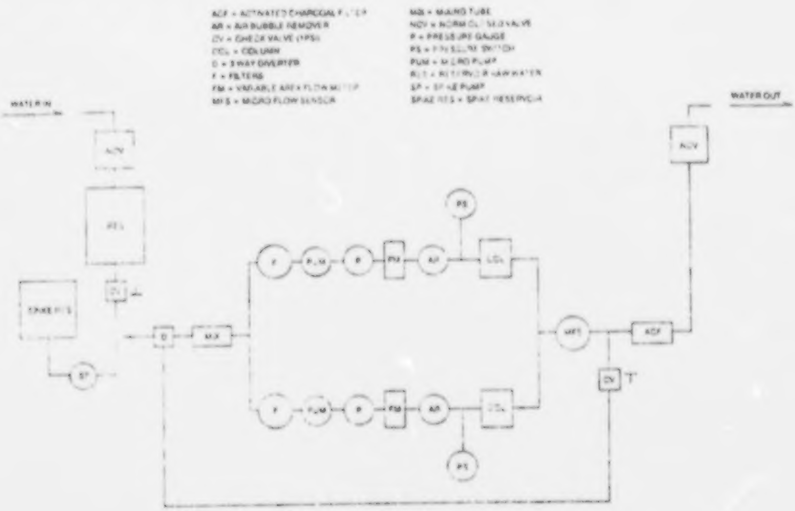
[a] Initial studies were centred on the determination of 2,3,7,8 - tetrachloro dibenzo-p-dioxin and related dioxins.

MARK II Automated Preconcentration Sampler (APS)

A schematic of the automated sampler is presented in diagram 1. The most important aspects of this design are A) the sampling stream is split into two identical duplicate streams after spiking, B) each stream is filtered and passed through an XAD resin column, C) all valves and safety features are automatically controlled, D) entire system is water proof from the inside out, and, E) no potential for release of spike or invalidation of samples with-out noticeable indication. At the present time the filters and resins are designed to be prepared in a clean laboratory environment and installed into the sampler. This can be performed either before transportation to the site or while the sampler is at a site. It follows that once a sample is collected, the filters and columns can be removed and new ones installed on site with-out compromising the integrity of the sample. Therefore, the sampler can be run continuously on site and the filters and columns transported to a lab for analysis.

Diagram 1 - Present Design of MARK II APS


ACF = ACTIVATED CHARCOAL FILTER
AR = AIR BUBBLE REMOVER
CV = CHECK VALVE (1PSI)
COL = COLUMN
D = 3 WAY DIVERTER
F = FILTERS
FM = VARIABLE AREA FLOW METER
MFS = MICRO FLOW SENSOR
MIX = MIXING TUBE
NCV = NORMALLY CLOSED VALVE
P = PRESSURE GAUGE
PS = PRESSURE SWITCH
PUM = MICRO PUMP
RES = RESERVOIR RAW WATER
SP = SPIKE PUMP
SPIKE RES = SPIKE RESERVOIR
WATER IN
WATER OUT
NCV
RES
CV
SPIKE RES
SP
D
MIX
F
PUM
P
FM
AR
COL
PS
MFS
ACF

Recovery Data

The development of the MARK II APS was accomplished through a joint project between MOE and Carleton university. Carleton's role in this collaboration was to provide the technical services required to design and construct the instrument as well as the labour required in the validation studies. MOE was responsible for the analysis of the samples generated in the validation studies as well as establishing the direction of these studies. As a result of this arrangement the volume of recovery data is limited to the area's of interest of MOE at the time of validation.

Stage I - Selected Dioxins

Dioxins represent the most commonly known hydrophobic class of pollutants who's toxicity and bioaccumulation potential make their presence unacceptable at extremely low levels[3]. Therefore, the initial work was concentrated on these substances. The recovery rates for these compounds were determined early in the development stage and thus disc filters were used rather than the Balston cartridge filters incorporated into the final MARK II design. This data is presented in Table 1. In order to test the Balston filters for interferences the filters were cut in half, one half was treated ultrasonically in toluene, and then dichloromethane. The other half was not treated. Each half was then spiked with 2.5 ng of ^{13}C-TCDD and ^{13}C-OCDD, soxhlet extracted for 16 hours with toluene and analyzed by MOE using their traditional clean-up procedure for GC/MS. These results are presented in Tables 2, 3, & 4.

Table 1 - Dynamic PCDD Spike in Treated Water

MOE submission number : C105198

Sample	Dynamic Spike TCDD	Dynamic Spike OCDD	Analytical Spike PCDD	Analytical Spike HCDD	
100 L treated water & 2.5 ng dynamic spike per column	42	38	54	72	A[*]
	42	45	61	73	B
	3	3	14	10	Backup

* A and B are the duplicate columns joined to a common backup column.

Table 2 - Recovery Data from Balston AH Tubular Filters

Congener	Pretreated Filter AH	Nontreated Filter AH
TCDD	[*]ND(70)	ND(50)
PnCD	INT	INT
HxCDD	ND(50)	ND(40)

Table 4 - Recovery Data from Balston AQ Tubular Filters

Congener	Pretreated Filter AH	Nontreated Filter AH
TCDD	ND(100)	ND(80)
PnCD	INT	ND(200)
HxCDD	ND(700)	ND(600)
HpCDD	ND(60)	ND(100)
OCDD	ND(90)	ND(300)
TCDF	ND(100)	ND(100)
PnCDF	ND(100)	ND(200)
HxCDF	ND(70)	ND(70)
HpCDF	ND(40)	ND(100)
OCDF	ND(90)	ND(100)
^{13}C-TCDD	51%	40%
^{13}C-OCDD	95%	80%

* ND - Not Detected (detection limit in ng/ul)
INT - Indeterminant

Stage II - Other Organics

A series of chlorinated compounds and polyaromatic hydrocarbons (PAHs) were selected from the "Drinking Water Priority Pollutant Parameter Analysis List", obtained from Laboratory Services Branch, MOE. The compounds were selected on the basis of 1) degree of chlorination, 2) degree of aromaticity, and 3) molecular weight. A description of the compound chosen is presented in table 5.

Table 2 -Continued- Recovery Data from Balston AH Tubular Filters

Congener	Pretreated Filter AH	Nontreated Filter AH
HpCDD	ND(80)	ND(70)
OCDD	ND(120)	ND(100)
TCDF	ND(100)	ND(100)
PnCDF	ND(200)	ND(50)
HxCDF	ND(80)	ND(60)
HpCDF	ND(100)	ND(80)
OCDF	ND(100)	ND(60)
^{13}C-TCDD	37%	45%
^{13}C-OCDD	52%	65%

* ND - Not Detected (detection limit in ng/ul)
INT - Indeterminant

Table 3 - Recovery Data from Balston AAQ Tubular Filters

Congener	Pretreated Filter AH	Nontreated Filter AH
TCDD	ND(100)	ND(40)
PnCD	ND(200)	ND(40)
HxCDD	ND(600)	ND(200)
HpCDD	ND(80)	ND(100)
OCDD	ND(100)	ND(100)
TCDF	ND(100)	ND(30)
PnCDF	ND(100)	ND(30)
HxCDF	ND(60)	ND(30)
HpCDF	ND(80)	ND(70)
OCDF	ND(100)	ND(100)
^{13}C-TCDD	49%	6%
^{13}C-OCDD	81%	12%

* ND - Not Detected (detection limit in ng/ul)
INT - Indeterminant

TABLE 5 TARGET ORGANICS SELECTED FOR PARTICULATE DISTRIBUTION SAMPLER STUDIES

TARGET COMPOUND	SELECTION CRITERIA		
	Aromatic(*) Aliphatic(-)	Mol.wt	Chlorination
Benzo(ghi)-perylene	*	276.3	No
Anthracene	*	178.0	No
Arochlor 1254	*	155+	Yes
1,2,4-Trichlorobenzene	*	181.5	Yes
Octachlorostyrene	(-)	380.7	Yes
2,4,5-Trichlorotoluene	(-)	195.5	Yes
Lindane	(-)	290.8	Yes
Mirex	(-)	545.6	Yes

Solutions (1 mL in methanol) of Anthracene, Arochlor 1254 and 1,2,4-trichlorobenzene were obtained from Supelco at a concentration of 200 ug/Ml. Lindane was purchased from Supelco at a concentration of 20 ug/Ml in 1 Ml of methanol. Benzo(ghi)perylene was also obtained from Supelco at a concentration of 200 ug/Ml in 1 Ml of dichloromethane. Octachlorostyrene, Mirex, 2,4,5-trichlorotoluene were all obtained in a neat form from National Health and Welfare.

In order to determine background levels and the effectiveness of the analytical techniques a series of

400 ng spikes were added to a method blank, and to the filters. The results are presented in table 6.

TABLE 6 RECOVERY OF ANALYTES FROM EXTRACTION AND SAMPLE WORKUP

Compound	Percent Recovery		
	Sample Workup Only	AAQ Filter	BQ Filter
1,2,4-trichlorobenzene	14	7	0
2,4,5-trichlorotoluene	81	46	3
Lindane	88	164	96
Anthracene	56	104	20
Octachlorostyrene	35	245	56
Mirex	248	170	71
Benzoperylene	0	0	0
PCBs	121	146	99

Anthracene d-10 was used as the internal standard at a concentration of 1 ng/uL.

These results indicate that the analytical method chosen was not acceptable for many of the compounds examined. The commercial lab performing the instrumental analysis also reported a large background of lindane, anthracene, PCB's, and in a few cases 2,4,5 - trichlorotoluene from the filters. It seems unlikely that so many of the compounds chosen for the testing would also be present as filter contaminants. Therefore, it is suspected that either contamination was introduced during the experiments or that the identity of the contamination was misinterpreted.

Dynamic spiking studies performed using deionized water as well as deionized water containing various levels of Illite (0-10 NTU) did indicate that the high molecular weight analytes (octachlorostyrene and mirex) were selectively retained on the Balston filters even when no particulate were present, while trichlorobenzene and trichlorotoluene was found predominately on the column. This strongly supports the application of analytical filtration as a potential method for preconcentrating selected analytes from large volumes of water as was proposed for dioxin analysis[8].

It is apparent that further testing is required to validate the MARK II APS. Universities function as service centres and as such rely on funding from government and private industry to survive, therefore, it is critical that this technology is transferred to an organization with access to the resources to provide this validation. At the present time Carleton is negotiating with Consumer Products Research and Testing (CPRT), an analytical and mechanical testing lab located in Nepean, Ontario for the commercial rights to the Mark II APS. This organization has the instrumental and technical expertise to validate the sampler on site. Funding is being solicited from NRC's, IRAP-M, and MOE's technology transfer fund to support validation and future development of the instrument.

Future Research

The potential of using filtration as an quantitative analytical technique, as well as, the lack of analytical grade filters capable of processing large volumes of turbid water, make filter research a primary objective.

CPRT is in the process of contacting the research and development divisions of the major filter producing companies to determine future filter trends and to get an insight into solutions to the present problems. Other area's of filter research includes treating the surface of glass fibre filters in order to increase the functionality and site selectivity to this surface.

It has been suggested that between .5 - 5 mg of residue can be collected from 100 L of drinking water by XAD-2 resin[9]. The determination of an analyte present at the 1 ppq in this sample then becomes, at best, a determination of 1×10^{-10} g of analyte in 5×10^{-4} g of residue contained on a 33 ml bed of XAD resin (an effective concentration of .2 ppm excluding resin contribution). This analysis is complicated by the fact that both the residue and analyte have been partitioned onto the hydrophobic resin and thus have a similar lipophilic nature. Therefore, suitable methods to selectively isolate compounds of interest are needed, or alternately methods which selectively preconcentrate the analytes from the water sample as suggested above may be required.

One technique that could be applied to selectively remove analytes from the residue is supercritical fluid extraction (SFE) using carbon dioxide (CO_2). A manipulation of the pressure and temperature of the SF effects the solvent strength of the CO_2 and thus solubility `bands' can be separated from the residue. This procedure can selectively leave the high molecular weight and boiling point solutes in the residue. This will facilitate the use of GC for subsequent analysis. Furthermore, once the analytes are contained within the supercritical stream, it may be possible to separate and determine the nature of the analyte. This will lead to the development of an automated on site analytical device with the capability of performing trace analysis with little or no operator input.

Conclusion

The isolation and preconcentration of trace hydrophobic organics from water systems is very complex task. The collection of a sufficient quantity of analyte for analysis is sometimes difficult. However, the most serious issue is the subsequent isolation of this analyte from the 'sea' of other species collected with it. Studies on the retention of selected organics onto glass fibre filters impregnated with binders suggests that some degree of selectivity can be obtained in the filtration process. Furthermore, associating selective ligands onto the filter infra-structure, may greatly simplify the subsequent cleanup procedure and thus reduce analysis time.

The incorporation of SFE technology into the MARK II APS will increase the selectivity of the extraction and represents the next step in developing an automated on-site detection system.

References

1. Kelly, K.E., International Approaches to Establishing Site Cleanup Levels : An Evaluation of Different Methods. 4th Conference on Toxic Substances. Proceedings. p 113-126. Ministry of Supply and Services Canada. Ottawa, 1990 Cat. No. En 40-11/4-1990F

2. Greaney, D.L., & Hope, W.B. Emergency Response Risk Assessment and Environmental Contamination Cleanup Criteria. 4th Conference on Toxic Substances. Proceedings. p 173-184. Ministry of Supply and Services Canada. Ottawa, 1990 Cat. No. En 40-11/4-1990F

3. Report of the Ministers' Expert Advisory Committee on Dioxins. Health and Welfare Canada / Environment Canada. Ottawa, November 1983.

4. National Research Council of Canada. Polychlorinated Dibenzo-p-Dioxins : Criteria for their Effects on Man and his Environment. Ottawa, NRCC No. 18574 of the Environmental Secretariat.

5. Kan, G., Extraction of Trace Organics with Amberlite XAD-7 and Sephadex A-25. p. 37-50. Preconcentration of Trace Organic Compounds from Large Volumes of Water. Workshop Proceedings Organized by Water Quality Branch and National Water Research Institute of Environment Canada. Burlington, 1987.

6. Brownlee, L.J., Shewchuk, C.S., Dowdall, J.E., & Hollebone, B.R. Project No. 329 PL : Refinement and Testing of a Preconcentration Sampler for Dioxins in Water. Final Report Submitted to MOE

7. Brownlee, L.J., Shewchuk, C., Bernard, C.E., & Hollebone, B.R. Project No. 420 G : Adaption of Water Preconcentration Techniques Developed for PCDD Analysis to other Target Organic Pollutants. Final Report. Submitted to MOE

8. Hollebone, B.R., Shewchuk, C., Brownlee, L.J., Dowdall, J.E., & Bernard, C.E., Development of Analytical Filtration as a Viable Method for the Monitoring of Polychlorinated-P-Dioxins in Raw and Treated Waters. To be submitted to Intern. J. Environ. Anal. Chem.

9. LeBel, G.L., Williams, D.T., Ryan, J.J., and Lau, B.P. *Evaluation of XAD-2 Resin Cartridge for Concentration / Isolation of Chlorinated Dibenzo-p-Dioxins and Furans from Drinking Water at the Parts-per-Quadrillion Level.* in Chlorinated Dioxins and Dibenzofurans in Perspective. Rappe, C. et al editors. Lewis Publishers. 1986.

PROGRESS ON THE DEVELOPMENT OF SPILL ANALYTICAL TECHNIQUES

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SUMMARY

Since 1980, the Environmental Emergencies Technology Division of Environment Canada has conducted projects to develop and evaluate analytical systems for spill response. Research has focused on several different levels. Level I is defined as a system that is pocket-portable, level II is a person-portable system, level III is a vehicle-portable system, level IV is a mobile laboratory, and Level V is a fixed laboratory. Some work has also been done for oil spill analysis and detection systems for ship-mounted application and extensive work on remote sensing detection means.

The focus of development has been on levels II and level III systems as applied to Canada's chemical spill priority list. It should be emphasized that analytical developments have focused on all three media; air, water and soil. Numerous papers, most of which appear in the bibliography, have presented the developments that have occurred over the past 9 years. This paper will be a summary of these with particular emphasis on more recent developments.

PERSON-PORTABLE ANALYTICAL SYSTEM

Early work focused on the development of person-portable systems for air contaminant measurement. The HNU and OVA instruments were chosen and modified by the addition of meter scale overlays to provide direct field measurement of 60 chemicals. The HNU meter scale overlays are now commercially-available. The HACH kit was evaluated as to its utility for measuring inorganic chemicals in water and adaptation was made for measuring these same substances in soil. Current work on the person-portable analytical system has dealt with 2 projects: first, continuing development of a person-portable analytical kit (PPAK) for analysis of organic compounds in water and soil and second, surveying and evaluation of available equipment. Each will be summarized briefly in the following section.

A) Person-Portable Analytical Kit (PPAK)

Work has been continuing on a Person Portable Analytical Kit for on-site analysis of chemicals in soil and/or water in which a single known chemical is involved. The existing system uses colorimetric and titrimetric techniques. The present kit can be used to quantify approximately 80 chemicals from the priority list in water and 60 in soil. The kit also has the capability for quantitative testing of approximately 85 non-priority chemicals in water. Information required for the determination of concentrations of environmental contaminants with the kit is detailed in Environment Canada Report EE-110 (Goldthorp et al., 1989). The information and tests in this report are currently being revised in accordance with recent protocol incorporating performance using different water samples (including saltwater) and different temperatures. Changes to the "Top 150 Spill Priority List"(1990) have prompted development and incorporation of tests for several contaminants which were not ranked in the previous listing (1981).

B) Survey/Evaluation of Portable Instrumentation for Field Use

A survey has been completed of available person-portable analytical systems which are directly field useable and provide quantitative results for a number of chemicals from Environment Canada's spill priority listing. The inclusion of instruments which satisfy the aforementioned criteria is based solely on information supplied by the manufacturers and distributors.

The information obtained for each instrument, or series of instruments, includes the full address of both the manufacturer and the Canadian distributor (if one exists), the name of the instrument and the detection method employed. Also included is a description of the instrument such as display characteristics, alarms, detection levels, response time, accuracy, operating conditions, power requirements and ranges for detectable compounds. The physical dimensions of weight and size as well as the price in Canadian dollars follow the instrument description. The survey has been published as an Environment Canada Report (Goldthorp, 1989).

In the survey, the listings are alphabetical according to the manufacturer. Charts which allow easy cross referencing are also included in the review. The charts allow the user to select a compound (listed alphabetically) and determine which instruments can be used for quantitative analysis. Charts are also available for selection of instrumentation using a specific analytical technique or for use when chemicals are found in different environmental media (namely air, water and soil).

As stated earlier, all the information in this survey is supplied by the manufacturers and distributors. Since the time of the release of the report, several developments have been made in the portable instrument industry. As advancements make electronic circuitry smaller and more efficient, there are more analytical techniques which can be adapted to a field-portable format. Many of the instruments which have been introduced or updated have been reviewed in the same manner as in the report of 1989. These addenda will be included in a forthcoming revision.

A detailed evaluation of selected instrumentation listed in this survey has been initiated and will include the following points:

-portability
-rapidity
-accuracy
-sensitivity

-simplicity of use, especially when wearing protective clothing (e.g. gloves, full face shield, etc.)
-simplicity of maintenance
-adaptability for use over a wide range of climatic conditions (e.g. temperature, humidity, etc.).

These instruments are evaluated following a set protocol. Instruments are submitted to standardized tests to determine their suitability for field-testing in Canadian conditions. Testing is done only for compounds listed as detectable by the manufacturer. Evaluations have been completed for many instruments. A compilation report of the results is forthcoming.

VEHICLE-PORTABLE ANALYTICAL SYSTEM

Work has been continuing on a vehicle-portable analytical system for on-site analysis of chemicals in air, soil, water and/or on various surfaces in which a single (known or unknown) chemical or a mixture of chemicals is involved. The development system has undergone major changes in the last year. The old gas chromatograph has been replaced by a Hewlett-Packard 5890 GC coupled to a HP5971A MSD (Mass Selective Detector). The 5890 GC is also equipped with a second injection port, column and flame ionization detector; a temperature programmable injection port ; an autoinjector; and a Chemstation. The latter is a DOS-based 386-personal computer which contains a library of 49,000 mass spectra which can be searched to aid in the identification of unknown pollutants. Retention indices are also needed to improve the reliability of identification.

Other equipment which has been installed in the vehicle includes a Suprex SFE/50 Supercritical Fluid Extraction instrument. This device employs carbon dioxide or other gases above their critical points to extract organic chemicals from solids. The unit enables extraction of samples in minutes (typically 30-min) at efficiencies approaching those achieved in days using conventional techniques. By selective extraction technique, background interference can be reduced and thus minimising sample workup time, which is an important consideration in emergencies situations.

Work is now under way to set up extraction and analytical parameters and calibrate the new systems. Additional work is required to develop sampling and concentration techniques for the commonly encountered matrices.

The new equipment will enable the vehicle-portable system to provide on-site analysis equivalent to that of a fixed laboratory with a turn-around time under 2 hours. In the cases where remedial actions must be taken in emergencies situations, the importance of providing meaningful data on-site cannot be over-emphasized.

SURVEY OF LABORATORY ANALYTICAL METHODS

A survey of analytical chemical methods which can be used in the vehicle-portable analytical systems for the quantitative analysis of chemicals in various environmental media, has been done (Vandenberg, 1989b). The survey is presented in a manual which is divided into three volumes with 410 analytical methods included. Volume 1 is a summary of Volumes 2 and

3. The first volume contains the indices for all the methods and a short summary of each method including such information as the procedure, the range and precision, the source and the environmental media to which the method is applied. Volume 2 contains the more detailed 135 methods for the analysis of chemicals in air. Volume 3 contains 170 methods for the analysis of chemicals in water and 105 methods for the analysis of chemicals in soil, also included are the sample collection and extraction methods. A summary of these methods is also available as Environment Canada manuscript report EE-115 (Vandenburg, 1989b).

BIBLIOGRAPHY

Bobra, A.M., "Development of Rapid Analytical Systems for Spill Response", Proceedings of the Sixth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario, 1989.

Bobra, A.M., "Development of a Vehicle-Portable Analytical System for Chemical Emergencies", Proceedings of the Second Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario, 1985.

Bobra, A.M., "Continuing Development of a Vehicle-Portable Analytical System", Proceeding of the Third Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario, 1986.

Goldthorp, M.D., J.T. Ruttan and M. Townshend-Colford, A Person-Portable Analytical Kit (PPAK) for the Analysis of Organic and Inorganic Compounds in Water and Soil, Manuscript Report EE-110, Environment Canada, Ottawa, Ontario, 1989.

Goldthorp, M., Review of Portable Instrumentation for Field Use, Manuscript Report EE-118, Environment Canada, Ottawa, Ontario, 1989.

Goldthorp, M.D., "Environment Canada's Person-Portable Analytical System: Recent Findings", Proceedings of the Fifth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario, 1988.

Lockwood, J. and R. Halman, "Person-Portable Systems for Multi-Media Analysis at Chemical Spill Sites", Proceedings of the First Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario, 1983.

Lockwood, J. and R. Halman, "Vehicle-Portable Systems for Multi-Media Analysis at Chemical Spill Sites" Proceedings of the First Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario, 1983.

Mills, W.J. and A. M. Bobra, "Continuing Development of a Vehicle-Portable Analytical System", Proceedings of the Fourth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario, 1987.

Ruttan, J.T., "Continuing Development of a Person-Portable Analytical System", Proceedings of the Fourth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario, 1987.

Streuker, L.C., "An Update on Environment Canada's Vehicle- Portable Analytical System", Proceedings of the Fifth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario, 1988.

Townshend-Colford, M., "Continuing Development of a Person-Portable Analytical System", Proceeding of the Third Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario, 1986.

Underdown, A. and M. Colford, "Development of a Person-Portable Analytical System", Proceedings of the Second Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario, 1986.

Vandenberg, D.J., Level III: Vehicle Portable Analytical System Operation Guidelines for Data Capture and Chemical Identification, Environment Canada unpublished report, 1989.

Vandenberg, D.J., A Manual of Analytical Methods for Pollutants in Air, Water and Soil, Vol. 1, 2 and 3, Environment Canada unpublished report,1989.

Vandenberg, D.J., A Manual of Analytical Methods for Pollutants in Air, Water and Soil, Environment Canada Manuscript Report Number EE-115, Ottawa, Ontario, 1988.

APPLICATION OF A MOBILE MS/MS AIR MONITORING SYSTEM DURING PCB INCINERATION IN SMITHVILLE, ONTARIO

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INTRODUCTION

Recent estimates show that nearly 120,000 tonnes of PCB waste containing more than 1% PCBs are stored at over 3,000 sites nationwide, including about 1,300 in Ontario. With scientific evidence suggesting that PCBs are hazardous to health, production of PCBs was banned in Ontario in 1977. The rapid increase in known and suspected contaminated sites, combined with PCB related incidents, has created a need for accurate real time, on-site analysis of ambient PCBs. A technique capable of measuring ppt (parts per trillion) levels of PCBs has been developed by the Ontario Ministry of the Environment. The method has been applied in the past decade to several PCB air monitoring surveys and emergency responses. This monitoring method, which combines an automated short term adsorber (ASTA) unit and a mobile mass spectrometer, provides real time measurements of selected PCBs (di- to penta-chlorobiphenyls). The initial method, developed in the early 80's, employed the use of a single quadrupole mass spectrometer (MS, TAGA 3000). In 1987 the Ministry upgraded this procedure by acquiring a mobile tandem quadrupole mass spectrometer (MS/MS, TAGA 6000). Advantages of the MS/MS system include minimization of chemical interferences, better sensitivity and lower detection limits. To date, the mobile TAGA 6000 has monitored several environmental emergencies and numerous contaminants, on-site, from a variety of industrial sources in Ontario. For quantification of PCBs, a heated nebulizer is used to inject controlled amounts of PCB liquid standards into the TAGA ion source. This technique allowed for calibrating the TAGA sensitivity thus establishing the limits of detection for PCBs. Typical detection limits for each PCB isomer group are of the order of 10 ng/m^3 (1 ppt). The ASTA/TAGA 6000 technique was field-tested for the first time in June 1990. It was recently used to monitor PCB emissions, both fugitive and point source, from a site in Smithville, Ontario, where a mobile incinerator was set up to thermally destruct approximately 8,500 tonnes of PCB-contaminated soil, metals and liquids. Upon commencement of PCB incineration in February 1991, the mobile TAGA 6000 conducted air monitoring in order to assure compliance of the Ministry's PCB guidelines for allowable ambient levels. In April, additional monitoring was carried out while continuous incineration of PCB contaminated soil was performed. This paper describes the mobile PCB monitoring technique and summarizes the results obtained in Smithville prior to and during incineration of PCBs. Incineration of PCBs in Smithville is expected to be completed in the fall of 1991 at which time the TAGA will conduct the final phase of the survey.

EXPERIMENTAL

ASTA Sampling System

For most chemical classes, the TAGA is extraordinarily sensitive for determining trace levels of organic contaminants. The absolute sensitivity for PCBs however is insufficient for real time detection relative to the low guideline set by the Ontario Ministry of the Environment for PCBs (450 ng/m^3 for a half-hour sampling period). Thus a simple sampling device is used to concentrate the volatile PCBs for immediate analysis by the mobile TAGA unit. This device, known as the automated short term adsorber (ASTA), was described in detail in a paper presented by Ng and De Brou (Proceedings of the Sixth Technical Seminar on Chemical Spills, Calgary, Alberta, June 5-6, 1989). Briefly, the ASTA, shown in Figure 1, consists of two OV-17 coated nichrome probes which can be rotated to place them alternatively in the ambient air stream or in the benzene/zero air stream. Species adsorbed to the probe are thermally desorbed into the TAGA's ionization chamber. The benzene serves as a chemical ionization reagent producing molecular PCB ions which are mass-analyzed by the TAGA. The time to complete one full cycle, or analysis, is 2 minutes and 8 seconds. A half-hour concentration of PCBs is determined by averaging 15 consecutive 2-minute adsorption/desorption cycles.

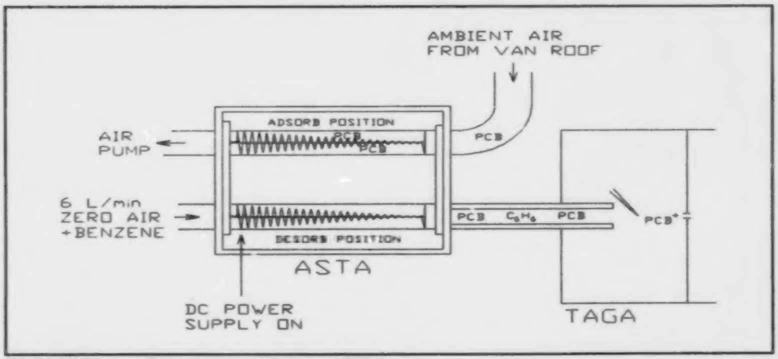


FIGURE 1. Schematic of the ASTA

TAGA 6000 MS/MS Analyzer

A schematic diagram of the TAGA 6000 is shown in Figure 2. The basic operation is governed by the principles of APCI (atmospheric pressure chemical ionization) tandem mass spectrometry. Parent ions, formed in the APCI region, pass through an orifice into the vacuum chamber where they are separated by the first quadrupole (Q1) and fragmented via collision with argon gas in the second quadrupole Q2 (RF only). The resultant fragments, or daughter ions, are analyzed by the third quadrupole (Q3).

The ion chemistry of volatile PCBs under APCI conditions is relatively simple: PCB molecules (M) undergo charge transfer reactions with benzene ions to yield molecular parent ions (M^+). Under collisionally activated dissociation (CAD) conditions, daughter ions at $(M\text{-}35)^+$, $(M\text{-}36)^+$ and $(M\text{-}70)^+$ (i.e. loss of Cl, HCl or Cl_2) are observed. Figure 3 shows the CAD spectra of di- and tri-PCB.

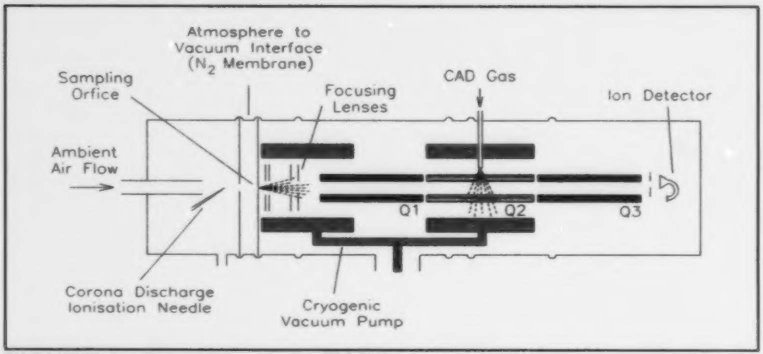

Atmosphere to
Vacuum Interface
(N_2 Membrane)
Sampling
Orfice
Focusing
Lenses
CAD Gas
Ion Detector
Ambient
Air Flow
Q1
Q2
Q3
Corona Discharge
Ionisation Needle
Cryogenic
Vacuum Pump

FIGURE 2. Schematic of the TAGA

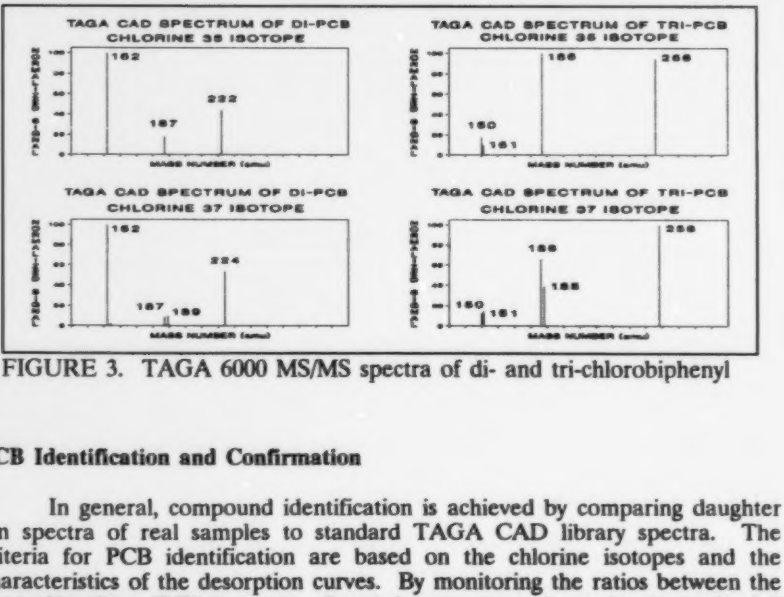
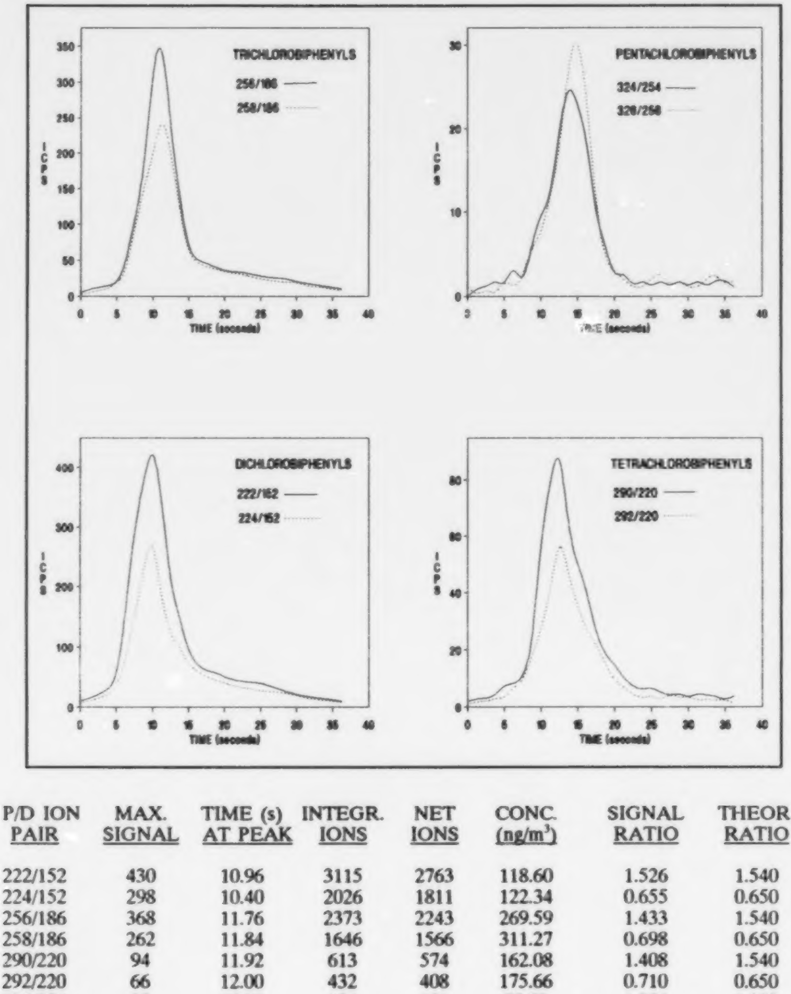


FIGURE 3. TAGA 6000 MS/MS spectra of di- and tri-chlorobiphenyl

PCB Identification and Confirmation

In general, compound identification is achieved by comparing daughter ion spectra of real samples to standard TAGA CAD library spectra. The criteria for PCB identification are based on the chlorine isotopes and the characteristics of the desorption curves. By monitoring the ratios between the parent/daughter (P/D) ion pairs of each isomer group, it can be determined if the parent ions have the correct number of chlorine atoms. Furthermore, times of desorption peaks, integrated areas, net PCB concentrations and signal to noise ratio for each isomer are determined. Typical desorption profiles for PCBs are shown in Figure 4.



P/D ION PAIR	MAX. SIGNAL	TIME (s) AT PEAK	INTEGR. IONS	NET IONS	CONC. (ng/m^3)	SIGNAL RATIO	THEOR. RATIO
222/152	430	10.96	3115	2763	118.60	1.526	1.540
224/152	298	10.40	2026	1811	122.34	0.655	0.650
256/186	368	11.76	2373	2243	269.59	1.433	1.540
258/186	262	11.84	1646	1566	311.27	0.698	0.650
290/220	94	11.92	613	574	162.08	1.408	1.540
292/220	66	12.00	432	408	175.66	0.710	0.650
324/254	25	13.36	136	121	93.89	1.224	1.025
326/256	33	15.36	111	99	87.55	0.817	0.976

FIGURE 4. Desorption curves of di-, tri-, tetra- and penta-chlorobiphenyl

The current computer programme allows for the simultaneous measurements of 4 PCB isomer groups (8 P/D ion pairs). Di- to penta-PCB are the most common isomers found in industrial applications. Also, PCBs with higher degrees of chlorination possess lower vapour pressures, consequently they are less likely to be detected by the ASTA/TAGA technique. Confirmation of PCB presence is based on the following criteria:

i. P/D isotope pair ratios - within ±10% of the theoretical values
ii. P/D isotope pair concentrations - within 20% for each isotope pair
iii. Desorption peaks - synchronous for each isotope pair
iv. Signal to noise ratios - greater than three for each desorption curve

PCB quantification

PCB aqueous standards are introduced upstream of the adsorbing probe via a heated nebulizer set at 300 °C. A schematic diagram of the nebulizer is shown in Figure 5. The configuration of the nebulizer ensures uniform sample atomization of controlled amounts of PCBs into the TAGA. The calibrant is injected into the nebulizer's capillary tube with a 1 mL syringe mounted on an infusion pump. The flow rates of PCBs are controlled by the speed of the pump. Vapourized PCBs from the standard are mixed with the ambient airflow, trapped by the adsorption probe for subsequent desorption and analysis. Flow rates 0 to 16 μL/min allowed a PCB concentration range of 0 to 400 ng/m^3 per isomer group to be generated in the APCI source.

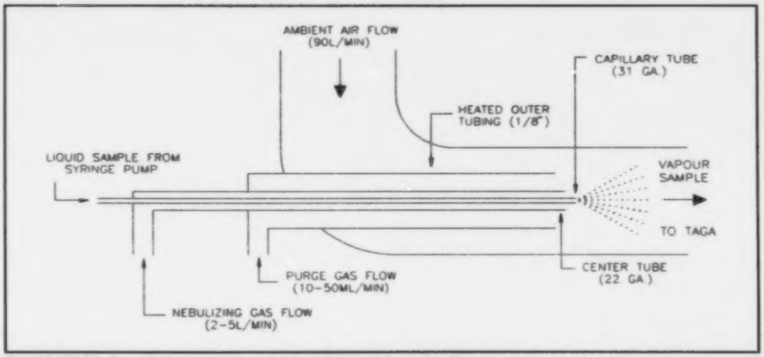


FIGURE 5. Schematic of the heated nebulizer

Six-point calibrations of PCBs are performed by simultaneously recording the responses of two parent/daughter (P/D) ions for four PCB isomers. Each PCB calibration level is repeated at least three times. The M+ and M+2 parent/daughter ion pairs are measured. Figure 6 shows examples of calibration plots for two congeners of the di- and tri-PCB isomer groups, both for the ^{35}Cl and ^{37}Cl isotopes. The response factors of the TAGA to a PCB isomer group is determined from the slope of the calibration plots. The standard deviations of the background, or upwind measurements, are used to determine the analytical detection limits.

During each survey day calibrations are performed at upwind locations to determine the response factors and the detection limits for each PCB isomer group. Also downwind ambient air samples are spiked periodically with an deuterated PCB internal standard (d_6 tetra-PCB, mass=296) to ensure that daily response factors are within their set limits. Typical detection limits for the di- to penta-chlorobiphenyls generally range from 5 to 15 ng/m^3 per isomer group.

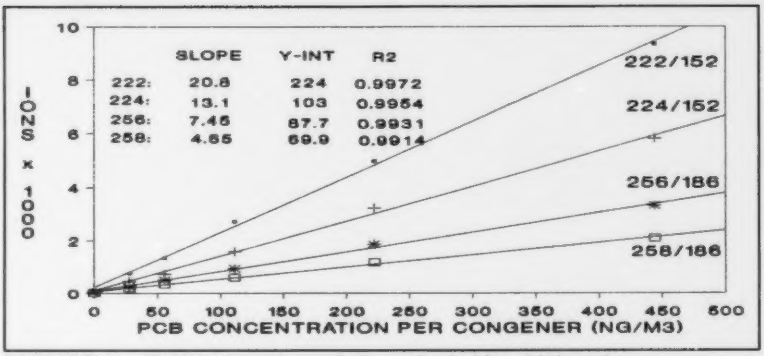


FIGURE 6. Calibration plots of di- and tri-chlorobiphenyl

SMITHVILLE PCB SITE

An area map of the PCB site in the Town of Smithville, Ontario, is shown in Figure 7. The PCB site covers an area of approximately 10,000 m^2. Within this area, which is fenced, there is a pile of contaminated soil, a water treatment facility, a shredder for contaminated metals, a containment building where drums of PCB liquid waste are stored, and Ensco's mobile incinerator. Smithville's stockpile included 160,000 litres of PCB liquids, 70 eighty-cubic feet vaults, 1,000 drums of PCB contaminated materials, 82 drained transformers and several hundred capacitors, magnets and other metallic objects. During incineration of contaminated materials, TAGA monitoring was performed at several locations in the immediate vicinity of the PCB site. The downwind monitoring sites are shown in Figure 7. Reference to these sites will be made often in the TAGA 6000 Results section. The Ensco incinerator is located in the north side of the PCB site.

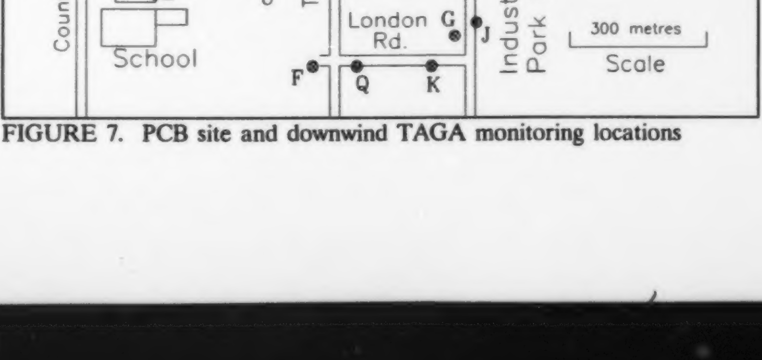

O
Spring Creek Rd.
H
B
D
C
I
N
M
L
Ensco
Incinerator
N
S
T
V
U
E
R
Smithville
PCB Site
County Rd. No. 14
Thompson Rd.
School
London Rd.
G
J
Industrial Park Rd.
300 metres
Scale
F
Q
K

FIGURE 7. PCB site and downwind TAGA monitoring locations

ENSCO INCINERATOR

A schematic diagram of the incinerator is shown in Figure 8. As illustrated in Figure 8, the incinerator destroys toxic organic compounds through two separate stages of burning; exposure to temperatures of 790 to 980 °C in a rotary kiln, and then 1260 to 1400 °C in a secondary combustion chamber. The intense heat from the secondary chamber is recovered in a boiler which generates steam to run air pollution control devices. Every step of the process is monitored and is designed to automatically shut it down if anything out of the ordinary is detected. Destruction of PCB contaminated soil and liquid wastes yields water, carbon dioxide and non-hazardous treated soil, which is further analyzed to ensure it is free of any toxics. If any are found, it can once again be cycled through the incinerator. TAGA monitoring was conducted during incineration to ensure compliance of the strict U.S. and Ontario's "Mobile PCB Destruction" requirement of 99.9999% destruction of PCBs in the waste.

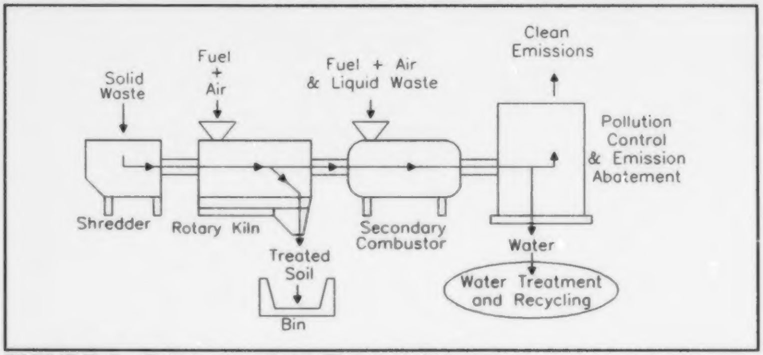


FIGURE 8. Schematic of the Ensco incinerator

TAGA 6000 RESULTS

Prior to Incineration

A survey was conducted in June 1990 to monitor the ambient air for selected PCBs prior to excavation of PCB contaminated soil and the relocation of capacitors and drums containing PCB liquid waste. During this survey PCB contaminated soil was covered with a plastic membrane to prevent rainwater from adding to the water table and to prevent PCB vapours and contaminated dust from moving off site. During this initial survey there was only one incidence where a trace quantity (13 ng/m^3) of tri-PCB was detected. A similar survey was conducted in January 1991 but this time the contaminated soil was not covered. The mobile incinerator, which had been assembled one week earlier, was not operating during this survey. However, some excavation and relocation of soil was performed. PCBs, less than 280 ng/m^3, were detected a few times only a short distance downwind of the contaminated soil and the building in which PCB liquid waste was stored.

During the Ensco Compliance Tests

In February 1991, a survey was conducted to determine PCB levels first prior to and during incineration of PCB contaminated solids and liquids. Six compliance tests were required under two different feed conditions in order to monitor stack emissions for regulatory approval. Three tests were conducted during incineration of PCB soil and liquid waste fuel and the other three were conducted during incineration of shredded capacitors mixed with PCB waste fuel. Solids included soil and capacitors which were shredded on site. Activities such as excavation of PCB contaminated soil and shredding metallic objects were performed several times during the survey.

Incinerator on Hot Standby

Figure 9 shows the half-hour average PCB concentrations measured downwind of the PCB site. During this monitoring period the incinerator was on "hot standby" meaning that the incinerator's kilns were maintained at operating temperatures but feeding PCBs for incineration was not performed. Thirty five half-hour average concentrations of PCBs were acquired downwind of the PCB site during February 4-9. PCBs were only detected on Spring Creek Road (Figure 7, Sites B, D and H), approximately 50 metres from the northeast corner of the Ensco tent where intermittent, mild solvent odours were evident.

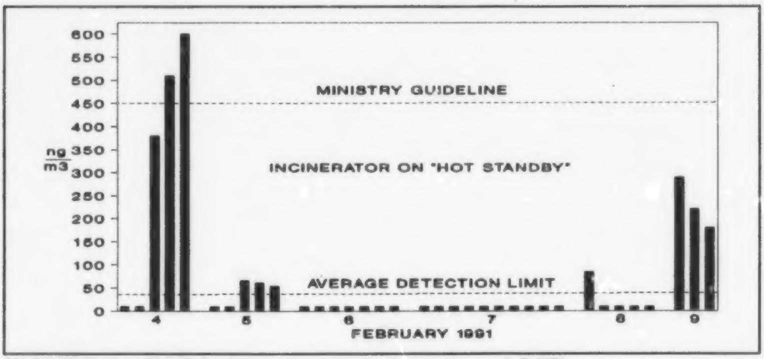


FIGURE 9. TAGA data prior to incineration of PCBs

Two half-hour average PCB concentrations of 510 and 600 ng/m^3 were slightly above the Ministry guideline of 450 ng/m^3 for total PCBs. Four half-hour averages of 380, 290, 220 and 140 ng/m^3 were below the Ministry guideline. Four half-hour averages showed traces of PCBs i.e., levels were between the detection limit (DL) and the quantitation limit (3.3xDL). Since the incinerator was on hot standby, it is reasonable to assume that the recorded PCB measurements corresponded to fugitive emissions from the PCB site. Potential sources of PCBs include the soil, the PCB containment building and the water treatment building. It is noteworthy that the capacitor shredder was also in operation on February 4 when the highest PCB levels were recorded.

Compliance Test I: Incineration of PCB Soil and Liquid Waste Fuel

On February 16, 19 and 20 contaminated soil (2 tons/hr) mixed with PCB liquid waste (roughly 1.6% total PCBs) was incinerated. Figure 10 (left) shows the results of 24 half-hour averages for PCBs measured at five different sites downwind of the incinerator. While sampling on Spring Creek Road at sites B or H (Figure 7), the plume from Ensco's stack was drifting above the TAGA, occasionally impinging on it. The highest PCB levels (150, 180 and 210 ng/m^3) were recorded on February 20 at site H. Note that one of these half-hour averages was measured while PCB soil feed had been halted. This result, along with observations made during the period of hot standby, suggests that the source of the detected PCBs was fugitive emissions from the PCB site, not from Ensco's incinerator.

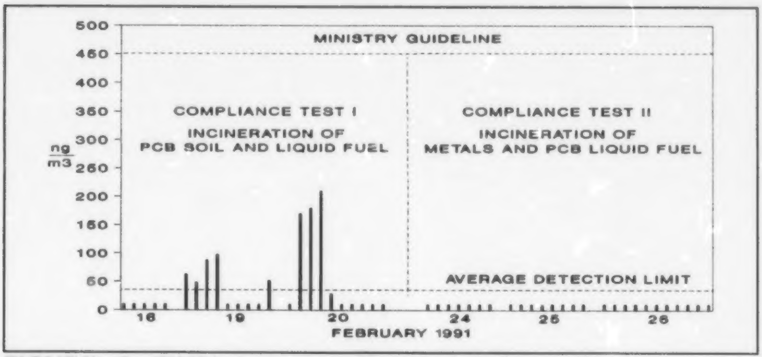


FIGURE 10. TAGA data during Ensco's compliance tests

Compliance Test II: Incineration of Metals and PCB Liquid Waste Fuel

On February 24, shredded capacitors were fed to the primary combustor at 500 lbs/hour and PCB liquid waste fuel to the secondary combustor at 5 lbs/minute. On February 25 and 26 the rate of PCB liquid fuel was increased to 17 lbs/minute. Twenty six half-hour averages were acquired at nine different downwind locations (Figure 7; sites E, M, N, U, V, Q, R, S, T). As shown in Figure 10 (right) PCBs were not detected above the TAGA's average detection limit (35 ng/m^3).

Incineration of PCB Contaminated Soil

In April 1991 the mobile TAGA returned to Smithville for additional PCB monitoring. This was necessary in order to confirm the results obtained during Ensco's compliance tests in February 1991. Twenty eight half-hour average concentrations of PCBs were acquired by the TAGA in April 15, 16, 17 and 19 while soil containing less than 0.58% PCBs was incinerated at a rate of about 4 tons/hour. During monitoring at sites B, D or H (Figure 7), mild solvent odours were present. At these sites PCBs were detected several times at levels as high as 300 ng/m^3 which is below the Ministry's guideline of 450 ng/m^3 as shown in Figure 11. These results are in agreement with those obtained in February during the compliance tests. The detected PCBs were due to fugitive emissions from the various PCB sources within the site, not from Ensco's incinerator.

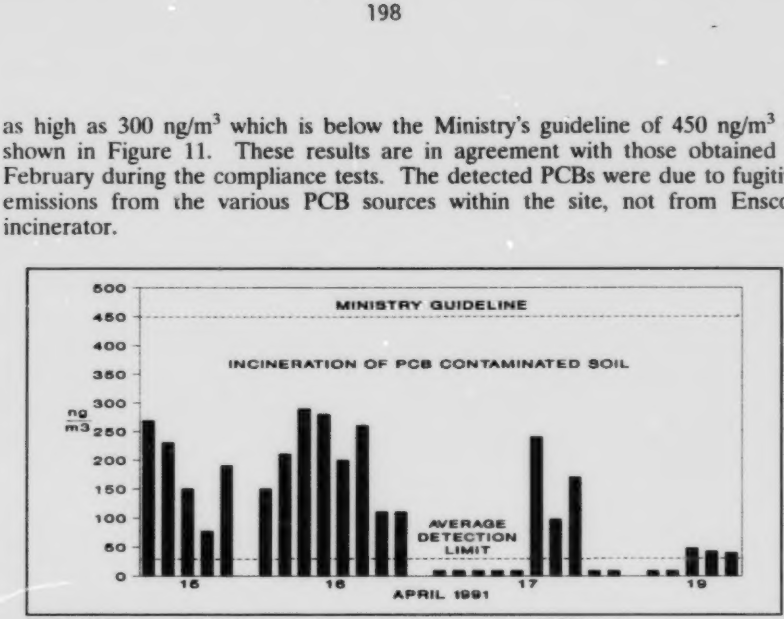


FIGURE 11. TAGA data during incineration of PCB soil

SUMMARY

Ambient PCB concentrations were measured by the TAGA under the following different conditions: with the contaminated soil being covered, exposed and excavated, prior to and during incineration of PCB waste. A total of 221 half-hour average PCB concentrations were recorded during the different phases of the survey. Monitoring locations were 30 to 1100 metres from the PCB site. Prior to excavation, when the PCB contaminated soil was covered with a plastic membrane, PCBs were not detected. Low PCB levels were recorded when the contaminated soil was exposed, excavated and relocated. On two occasions, PCB measurements exceeded the Ministry guideline of 450 ng/m^3 although PCB incineration was not being performed. Several times PCB levels were in the range 100 to 400 ng/m^3. PCBs were measured above the TAGAs quantitation limit (approximately 100 ng/m^3) at distances not exceeding 150 metres from the PCB site, at times when mild solvent odours were recognizable. During incineration the plume from Ensco's stack was always visible. Several times while monitoring, the plume was drifting just over the TAGA and occasionally was impinging on it. During such episodes, however, neither the odour intensity nor the PCB levels were elevated. The data indicate that PCBs detected both prior to and during incineration were due to fugitive emissions from the PCB site, not from the stack of the Ensco incinerator. Nevertheless, 99.1% of all PCB levels recorded by the TAGA 6000 were below the Ministry guideline of 450 ng/m^3 for a half-hour average concentration of total PCBs.

DETERMINATION of MERCURY EXPOSURE LEVELS IN INDOOR AIR from INTERIOR LATEX PAINT CONTAINING PHENYLMERCURIC ACETATE

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The Environmental Response Team (ERT) of the United States Environmental Protection Agency (USEPA) was established in October, 1978 to provide technical assistance to other branches of the EPA, as well as other United States and foreign government agencies in the area of environmental emergencies, such as chemical releases and uncontrolled hazardous waste sites. As part of its responsibility, the ERT is responsible for collecting air samples for a wide variety of chemical constituents.

In August 1989, the symptoms of acrodynia, a form of mercury poisoning, developed in a four-year-old boy in Michigan ten days after the inside of his home was painted with 64 liters of interior latex paint containing 940 mg of phenylmercuric acetate (PMA) per liter of paint. At that time, the EPA recommended limit was 300 mg or less per liter. PMA is used by many paint companies as a preservative to prolong the shelf life of interior latex paint.

In November 1989, the ERT was requested by the Agency for Toxic Substances and Disease Registry (ATSDR) and EPA Region V to assist the Center for Disease Control (CDC) in determining whether the recent use of that brand of paint containing PMA would cause elevated levels of mercury vapors.

METHODS

The ERT collected air, paint and vacuum bag samples from 19 homes painted with this paint between June 1 and October 28, 1989, where the painters had either used 11 or more liters of paint or painted three or more rooms. For controls, samples were collected from nine homes not recently painted with paint containing PMA. Personnel from CDC collected urine samples from the families living in the homes sampled to determine uptake.

The sampling occured in three phases. During Phase I, the screening phase, sampling was performed to determine whether levels of mercury in the recently painted homes were at elevated levels to warrant a concern. During Phase II, the control phase, sampling was performed to ascertain the if levels of mercury in homes painted with PMA paint were above levels from homes not painted with this type of paint. During Phase III, sampling was conducted to determine if the levels of mercury in the homes were changing.

The indoor air samples were collected and analyzed following a modification of NIOSH method 6009. Samples were collected on hopcalite (hydrar) tubes using personal sampling pumps over a twelve-hour period at a flow rate of 0.5 - 1.0 liters/min. in order to obtain a minimum detection of limit 0.3 ug/m ^{3}. The samples were collected at a height associated with a person's breathing zone in each of the rooms painted.

The paint, vacuum-cleaner, and urine samples were analyzed by cold-vapor atomic absorption. The limit of mercury detection was < 2.0 ug per liter for paint, 2.0 ug per kilogram for dust, 0.1 to 0.2 ug per liter for urine.[1]

RESULTS

Paint samples were obtained from all the homes of exposed families. The median mercury content of the paint in the 29 cans sampled was 0.8 g per liter. Paint in 26 cans (90%) contained more than 0.3 g of mercury per liter. Paint samples from six (60%) control homes did not contain mercury. The vacuum-cleaner-bag dust samples taken from seven of the mercury painted houses had a higher mercury content (median, 38 mg per kilogram; range 5.3 to 54 mg/kg) than those from the control households (median 3.4 mg/kg; range 1.9 to 13 mg/kg; $P=0.05$).[2]

The air sampling results for the mercury painted houses and the control homes are summarized in Tables 1

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[1]. Agocs M, Etzel R, eds, Mercury Exposure From Interior Paint, The New England Journal of Medicine Oct. 18, 1990; Vol. 323 No.16: 1096-1101.

[2]. ibid

TABLE 1. PHASE I SAMPLING RESULTS
DETROIT RESIDENTIAL SURVEY
DETROIT, MI

Residence	Real-Time Date in mg/m^3	Location	Hopocolite (Hydrar) Date in ug/m^3
1. 4125 Crooks Royals Oaks, MI	.001	Living Room	0.8
2. 31654 Rosenbush Warren, MI	.002	Locked Room	5.8 2.0 (DUP)
3. 24712 Harden Southfield, MI	.002	Family Room	0.8
4. 24725 Harden Southfield, MI	.000	Family Room	1.0
5. 33687 Heritage Hills Farmington Mills, MI	.001	Office	2.7
6. 4936 Champlain Cir. West Bloomfield, MI	.000 .000	Locked Room Bedroom	2.0 5.0
7. 4215 N. Willoway Ct. Bloomfield Hills, MI	.001	Den	1.0
8. 5578 Wildridge Lane West Bloomfield, MI	.001	Spare Room	0.2
9. 1581 Oak Grove Walled Lake, MI	.022	Bath	10.0
10. 7001 Heather Heath West Bloomfield, MI	.003	Bedroom	2.8
11. 25260 Cedar Grove West Bloomfield, MI	.002	Living Room	3.1
12. 2355 Bedford Bloomfield Hills, MI	.001	Living Room	0.6
13. 29718 Robert Dr. Livonia, MI	.000	Living Room	<0.3

14. 3261 Alderdale Sterling Heights, MI	.007	Girl's Room	4.2
15. 3614 Charlwood Rochester Hills, MI	.000	Guest Room	0.6
16. 4112 Thorney Rochester Hills, MI	.000	Bath	0.6
17. 312 Tanglewood Rochester Hills, MI	.010	Living Room	8.3
18. 19784 Poinciana Redford, MI	No Jerome Readings	Living Room	<0.3
19. 23881 Condon Oak Park, MI	.006	Office	1.0
20. 28444 Kendallwood Farmington Hills, MI	.002	Living Room	2.0 1.0 (DUP)
21. 32189 Rush Garden City, MI	.002	Child's Room	0.8
22. 6253 Lathers Garden City, MI	.010	Bedroom	5.6

TABLE 2. PHASE II SAMPLING RESULTS
DETROIT RESIDENTIAL SURVEY
Nov. 28-29, 1989

Residence	Location	Real-Time Room Average in mg/m^3	Hopcalite (Hydrar) in ug/m^3
1. 2920 Town Hill, Troy, MI	Guest Room	.000	<.01
2. 5144 Shrewsberry Troy, MI	Guest Room	.000	<.01
3. 11425 Crown Dr. Sterling Heigths, MI	Girls Room	.000	<.01
4. 1812 East Madge, Hazel Park, MI	Family Room	.000	<.01
5. 279 Fielding, Ferndale, MI	Dinning Room	.000	<.01
6. 3457 Innsbrook, Rochester, MI	Dinning Room	.000	<.01
7. 1781 Beverly, Sylvan Lake, MI	Boy's Room	.000	<.01
8. 3252 Bulwer Keego Harbor	Living Room	.000	<.01
9. 7011 Heather Heath West Bloomfield, MI	Family Room	.000	<.01

TABLE 3. PHASE III MONITORING AND SAMPLING DATA
DETROIT RESIDENTIAL SURVEY
APRIL 16-17, 1990

Residence	Location	Real-time Data in mg/m^3 (1)	Hopcalite Data in ug Hg/m^3 Air
1. 33687 Heritage Hills Drive Farmington Hills, MI	Office	CBZ=.000 WBZ=.000 WBB=.000	0.27
2. 29718 Robert Dr. Livonia, MI	Living/Dining Room	CBZ=.000 WBZ=.000 WBB=.000	ND
3. 5260 Cedar Grove Ct. West Bloomfield, MI	Living Room	CBZ=.000 WBZ=.000 WBZ(2)=.000	0.56
4. 28444 Kendallwood Farmington Hills, MI	Child's Room	CBZ=.000 WBZ=.000	1.89
5. 1581 Oak Grove Dr. Walled Lake, MI	Bathroom	WBZ=.000 WBB=.000	0.89
	Family Room	WBZ=.000 WBB=.000	0.79
6. 31654 Rosenbush Warren, MI	Spare Room	CBZ=.000 WBB=.000	1.06
7. 24725 Harden Ave. Southfield, MI	Family Room - house vacant	CBZ=.000 WBZ=.000 WBB=.001	0.11
8. 24712 Harden Ave. Southfield, MI	Family Room	WBZ=.001 WBB=.001	0.79
9. 4936 Champlain Cir. West Bloomfield, MI	Boy's Room	CBZ=.000 WBZ=.000 Duplicate	N/A(3)-Volume Unknown 0.75,1.04

10. 5578 Wildridge Lane West Bloomfield, MI	Study - was vented	CBZ=.001 WBZ=.001 WBZ(2)=.001	0.31
11. 7001 Heather Heath West Bloomfield, MI	Study - walls were replaced & repainted	CBZ=.000 WBZ=.000 WBB=.000	0.10
12. None	Lot Blank		ND
13. None	Lot Blank		ND
14. None	Field Blank		ND
15. None	Field Blank		ND
16. 1781 Beverly (C)(4) Sylvan Lakes, MI	Boy's Room	CBZ=.000 WBZ=.000 WBB=.000 Duplicate	ND ND
17. 4125 Crooks Royal Oaks, MI	Living Room	CBZ=.006 WBZ=.000 WBB=.000	0.61
18. 2920 Town Hill (C)(4) Troy, MI	Spare Room	CBZ=.000 WBZ=.000 WBB=.000	ND
19. 5144 Shrewsbury (C)(4) Troy, MI	Spare Room	CBZ=.009 WBZ=.000 WBB=.000	ND
20. 11425 Crown (C)(4) Sterling Heights, MI	Girl's Room	CBZ=.000 WBZ=.000 WBB=.000	0.04
21. 4112 Thorney Rochester Hills, MI	Bathroom	CBZ=.000 WBZ=.000 WBB=.000	0.32
22. 312 Tanglewood Rochester Hills, MI	Living Room	CBZ=.003 WBZ=.000 WBB=.000	0.9

23. 3614 Charlwood Rochester Hills, MI	Guest Room	CBZ=.000 WBZ=.000 WBB=.000	0.51
24. 2335 Bedford Bloomfield Hills, MI	Living Room	CBZ=.004 WBZ=.000 WBB=.000	0.19
25. 4215 Willoway Ct. Bloomfield Hills, MI	Den	CBZ=.000 WBZ=.000 WBB=.000	0.26
26. 3252 Bulwer (C)(4) Keego Harbor, MI	Living Room	CBZ=.000 WBZ=.000 WBB=.000	ND

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(1) Readings are averages of three readings taken in one location (see Data Sheet Appendix B). Central Breathing Zone (CBZ), Wall Breathing Zone (WBZ), Wall Base Boa (WBB).

(2) Laboratory detection limit = 0.02 ug Hg/tube. ND is < or = 0.02 ug Hg/tube.

(3) N/A indicates not applicable.

(4) (C) indicates a designated "control" house.

thru 3. The mercury concentration in the air samples collected from the mercury painted houses were significantly higher than the control houses ($P<0.001$). Mercury was only detected in the homes painted with paint containing PMA. The median air concentration was 2.0 ug/m^3. The mercury concentration ranged from < 0.1 ug/m^3 to 10 ug/m^3. Among the exposed houses, the concentration of mercury vapors were significantly higher in the homes that had more rooms painted, or had been painted more recently, or had windows open for only a few hours a day, or were newer[1].

The urinary mercury concentration, both adjusted and unadjusted for creatinine were significantly higher among exposed persons than among the unexposed ($P<0.001$).[1] The median adjusted urinary mercury concentration was 4.7 nmole per millimole of creatinine in the 65 exposed persons (range 1.4 to 66.5) and 1.1 nmole per millimole of creatinine in the 28 unexposed persons (range, 0.02 to 3.9).[2] Fourteen exposed persons (22 %) had urinary mercury concentration > 100 nmole/liter, and 45 exposed (69 %) had levels > 50 nmole/liter. Only one exposed person (4 %) had a mercury level > 50 nmole/liter.[2]

There was poor correlation between urinary mercury levels and the levels of mercury found in the air samples collected at the residence ($r=0.17$). The correlation was, however, higher among exposed persons who were younger, applied the paint themselves, spent more hours in the house, and lived in homes painted less recently ($r=0.29$).

DISCUSSION

We found that homes recently painted with one brand of interior latex paint containing PMA had significantly higher levels of mercury in the indoor air than the control homes. People living in recently painted homes had significantly higher urinary mercury levels than those people living in the control homes.

The median indoor mercury air level determined in this study in the exposed household (2 ug/m^3) exceeded the acceptable residential concentration of 0.5 ug/m^3 suggested by the Agency for Toxic Substances and Disease Registry[3] and was more than 600 times higher than the average outdoor air concentration for mercury in the Detroit area.[1] The measurement of mercury in the indoor air of exposed homes were taken an average of one month after painting had been completed. The levels would probably be higher during and immediately after painting. Investigators have measured 200 ug/m^3 during the application of paint indoors.[4] After 30 minutes, with the application of paint containing 200 ug of mercury per liter of paint resulted in 170 ug/m^3 mercury in the air.[5] The National Institute for Occupational Safety and Health (NIOSH) recommends a mercury level of 50ug/m^3 (a 10-hour time weighted average) not be exceeded in a work area.

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[3]. Office of Health Assessment, ATSDR. Preliminary Health Assessment. Charleston, Tenn: Olin Chemical Company, 1988.

On June 29, 1990, the EPA announced that compounds containing mercury could no longer be lawfully added to interior latex paint after August 20, 1990. This decision represented a voluntary end to the use of mercury in paint and was made jointly with the National Paint and Coating Association and the manufactures of the mercury compound. Interior paint containing mercury that was manufactured before August 20, 1990, may still be sold.

ACKNOWLEDGEMENT

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DISCLAIMER

The mention of trade names or commercial products in this paper does not constitute an endorsement or recommendation for use by the EPA. Contents of this paper do not necessarily reflect the views and policies of the EPA.

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[4]. Jacobs MB, Goldwater LJ, Absorption and Excretion o Mercury in Man, VIII, Mercury Exposure from House Paint - Controlled Study on Humans. Arch Environ Heath 1965; 11:582-7.

[5]. Clarkson TW, Magos L, Greenwood MR, The Transport o Elemental Mercury into Fetal Tissues. Bio Neonate 1972; 21:239-44

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OMITTED

INTENTIONALLY

A NEW CHEMICAL SPILL PRIORITY LIST

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INTRODUCTION

In 1979, the Environmental Emergencies Branch embarked on an accelerated program to improve the response and countermeasures technology for spills of materials other than oil. As an essential part of this program, a methodology was devised to develop a priority list of chemicals. A list of 150 chemicals was compiled of hazardous materials that had significant potential as spills in Canada. This list was then used to develop specialized countermeasures, analytical techniques and spill manuals. Individual manuals called EnviroTIPS were prepared for the first 50 priority substances. Tests of the utility of the priority list showed that a large portion of the spills were those of the higher priority substances.

Statistical spill data are extremely useful for setting priorities and identifying project needs for spill prevention and preparedness. This was recognized in 1972 and a database was developed to consolidate all Canadian spill data. This database is known as NATES, short for National Analysis of Trends in Emergencies System.[1] Table 1 shows the type of data that can be extracted from the system for chemical spills alone. This table covers chemical spills from 1974 to 1984 and was used to develop the current priority list. The NATES database now contains data on over 40,000 spill events. About 70% of these spill events are related to oil and petroleum products. About 20% involve wastes and aggregate materials. Only about 10% involve the spillage of "pure" chemicals.

THE FIRST SPILL PRIORITY LIST

The first spill priority list was developed in 1980.[2,3] Lists of the top 10, 50 and 150 were developed. Table 2 is the 1980 priority list of 150 substances. Several mathematical approaches to the development of the priority list were tried, however it was found that a simple ranking of supply volume, reported spill frequency, historical spill volumes and toxicity could result in a satisfactory list. The main objective was to identify the minimum number of chemicals that would account for the maximum number of spills. The use of the list would be as noted above, to act as a focus for the development of countermeasures, analytical methods and spill manuals.

Table 1 SPILL OF CHEMICALS 1974-1984 Data from NATES

CHEMICAL	NUMBER OF SPILLS	VOLUME(t)
Acetic acid	9	73.25
Acetic anhydride	8	1.51
Acetone	4	9.93
Acetylene	1	0.01
Acrylonitrile	1	4.6
Aldrin	2	1.32
Aluminum phosphate	3	8.50
Aluminum silicate	1	10.5
Aluminum sulfate	9	122.2
Aminocarb	12	55.77
Ammonia,anhydrous	107	466.12
Ammonium chloride	1	0.7
Ammonium hydroxide	15	127.64
Ammonium nitrate	63	4237.64
Ammonium phosphate	5	144.4
Ammonium stearate	1	0.1
Ammonium sulfate	8	261.7
Aniline	1	0.1
Arsine	1	0.0
Asbestos	15	310.47
Atlox	1	0.2
Atrazine	2	0.85
Azinphos-methyl	1	0.0
Barban	1	0.01
Barium sulfate	1	820.0
Benzene	12	13.76
Benzoic acid	2	34.5
Benzotrifluoride	1	50.48
Bromoform	1	0.01
Butanol	1	2.23
Butyl formate	1	0.04
Calcium arsenate	1	0.05
Calcium carbide	1	1.8
Calcium chloride	20	3678.84
Calcium cyanide	1	0.09
Calcium fluoride	1	1.00
Calcium hydroxide	17	360.13
Calcium hypochlorite	4	17.41
Calcium nitrate	1	1.8
Calcium oxide	12	530.94
Calcium phosphate	3	103.6
Carbaryl	2	69.60
Carbofuran	4	0.06
Carbon dioxide	1	0.0
Carbon tetrachloride	1	1.8
Cesium 137	3	0.00
Chlordane	2	0.00

Table 1 ctd. Spills of Chemicals 1974-1984

CHEMICAL	NUMBER OF SPILLS	VOLUME(t.)
Chlorhydrin	1	0.8
Chlorine	36	120.97
Chlorine dioxide	2	0.3
Chloroaniline	1	0.5
Chorodifloromethane	1	0.27
Chlorophenol	1	0.04
Chromic acid	7	8.82
Cobalt hydroxide	1	5.1
Cobaltous nitrate	1	0.9
Copper cyanide	1	2.2
Copper oxide	1	0.0
Copper sulfate	5	22.9
Cresols	2	12.7
Cresylic acids	2	0.07
Cyanides	7	2.0
Cyanogen bromide	1	0.00
Cyclohexane	1	0.11
Cyclohexylamine	1	0.07
2,4-D	37	129.03
Decyl octyl phthalate	1	0.1
Diallate	3	0.08
Diazinon	4	0.23
Dicamba	2	0.17
Dichlorvos	1	0.1
Dieldrin	1	0.00
Diethanolamine	1	0.2
Diethyl methyl amine	1	0.0
Diethylamine	2	1.8
Dinitroamine	2	0.0
Dinoseb	1	0.91
Diphenyl	1	1.3
Diphenyl amine	1	0.03
Diphenyl oxide	1	1.5
Diquat	2	0.0
Ethanol	3	50.79
Ethyl acrylate	3	1.13
Ethyl amine	1	1.3
Ethyl benzene	4	0.79
Ethyl chloride	2	0.2
2-Ethylhexanol	1	100.7
Ethyl mercaptan	6	0.01
Ethylene	2	178.5
Ethylene dichloride	1	781.0
Ethylene glycol	31	593.83
Fenitrothion	49	100.47
Ferric chloride	8	1004.47
Ferric hydroxide	2	5.0
Ferric oxide	5	22.7
Ferric sulfate	1	0.5

Table 1 ctd. Spills of Chemicals 1974-1984

CHEMICAL	NUMBER OF SPILLS	VOLUME(t.)
Ferrous sulfate	1	21000.0
Flamprop-methyl	3	0.16
Fluoboric acid	1	0.0
Formaldehyde	10	41.05
Formic acid	1	0.2
Glyphosate	1	0.00
Heavy water	2	22.2
Hexane	5	8.03
Hydrazine	3	4.52
Hydrochloric acid	123	3335.13
Hydrofluoric acid	5	0.68
Hydogen peroxide	7	0.71
Iridium 192	1	0.0
Isopropanol	4	9.27
Lead oxide	2	2.1
Lignin sulfonate	5	181.97
Lindane	1	0.00
Lithium bromide	1	0.13
Magnesium hydroxide	1	10.5
Magnesium oxide	1	5.0
Malathion	7	0.29
Maleic anhydride	1	2.8
Maneb	1	1.28
MCPA	5	0.91
Methomyl	1	0.0
Methyl ethyl ketone	4	7.66
Methyl ethyl ketone peroxide	1	0.0
Mercuric sulfide	1	29.9
Mercury	11	19.90
Methyl methacrylate	3	3.40
Methane	1	0.06
Methanol	18	734.75
Methoxychlor	1	0.05
Methyl chloride	2	2.5
Methyl hexyl ketone	1	0.94
Methylamine	1	5.3
Methylene chloride	4	6.15
Naphthalene	3	6.40
Neopentyl glycol	1	0.01
Nickel carbonyl	1	0.3
Nitric acid	40	139.60
Nitroaniline	1	0.00
Nitrogen dioxide	3	0.00
Nitrogen	3	1.85
Nitrous oxide	1	0.6
Nonane	1	0.01
Nonylphenol	2	8.78
Oxygen,liquified	5	24.19

Table 1 ctd. Spills of Chemicals 1974-1984

CHEMICAL	NUMBER OF SPILLS	VOLUME(t.)
Paraquat	2	43.61
Parathion	1	0.01
Phosphamidon	8	15.6
Pentachlorophenol	19	109.34
Perchloroethylene	10	15.50
Phenolsulfonic acid	2	22.6
Phenol	10	14.2
Phenylmercury acetate	1	0.01
Phenyl diamine (para)	1	0.0
Phosphorus	16	45.52
Phosgene	1	0.0
Phosphorus pentoxide	1	0.6
Phosphine	1	0.00
Phosphoric acid	12	36.2
Phthalic anhydride	3	7.2
Picloram	3	0.53
Polychlorinated biphenyls	334	89.24
Potassium aluminate	1	0.7
Potassium carbonate	1	100.0
Potassium chloride (potash)	31	11836.01
Potassium cyanate	1	0.01
Potassium hydroxide	2	1.2
Potassium permanganate	4	9.80
Propylene chlorohydrin	1	8.91
Propionic acid	1	2.0
Propylene	1	9.1
Proplylene glycol	1	8.3
Propylene oxide	2	22.02
Pyridine	2	0.01
Sodium,metal	1	0.5
Sodium aluminate	1	14.3
Sodium arsenite	1	0.0
Sodium borohydride	1	4.5
Sodium carbonate	3	25.04
Sodium chlorate	23	7676.94
Sodium chromate	1	0.02
Sodium cyanide	3	82.6
Sodium dithionite	2	28.9
Sodium fluoride	1	0.2
Sodium hydroxide	92	8225.74
Sodium hydrosulfide	2	2.28
Sodium hypochlorite	11	58.05
Sodium nitrate	1	2.5
Sodium silicate	1	3.8
Sodium stearate	1	0.05
Sodium sulfite	4	29.15
Sodium thioglycolate	1	0.2
Styrene	24	5001.29
Sulphur	68	69720.01

Table 1 ctd. Spills of Chemicals 1974-1984

CHEMICAL	NUMBER OF SPILLS	VOLUME(t.)
Sulphur chloride	3	3.51
Sulphur dioxide	16	89.5
Sulphuric acid	155	13362.47
Stannic chloride	1	0.0
Sulfuryl chloride	2	4.4
2,4,5-T	2	0.24
Terephthalic acid	1	0.18
Terphenyl	2	1.06
Tetraethyl lead	4	71.9
Tetrahydronapthalene	1	0.09
Thallium sulphate	1	0.03
Thioglycolic acid	1	0.0
Thiram	1	0.3
Titanium dioxide	2	0.5
Toluene 2,4-diamine	2	11.42
Toluene diisocyanate	7	1.10
Toluene	13	105.21
Tributylphosphate	1	0.3
Trichlorfon	3	2.6
Trichloroethane	4	0.81
Trichloroethylene	1	0.13
Triethanolamine	1	0.19
Trifluralin	9	4.59
Trimethyl amine	1	1.5
Trimethylene bromide	1	0.4
Trinitrotoluene	1	17.0
Uranyl nitrate	3	0.21
Vinyl acetate	8	7.41
Vinyl chloride	31	183.39
Xylenes	14	46.59
Yellow cake	1	0.21
Zinc bromide	1	0.38
Zinc chloride	1	12.8
Zinc cyanide	1	0.2
Zinc oxide	3	54.5
Zinc phosphate	1	0.9
Zinc stearate	1	0.0
Zinc sulphate	3	68.4

The first priority list was successful in that a few number of chemicals could account for many spills. The first 10 chemicals accounted for 37% of the reported spill events by number, 83% of the spill volume, and 50% of the volume of chemical supply in Canada. Figure 1 shows the utility of the list as applied to the spill history of 1980. The "utility" is a mathematical term to describe the usefulness or applicability of a particular formula or in this case the results of a mathematical exercise.

Table 2 1980 List of The 150 Top Priority Chemicals

1,1,1-Trichloroethane
1,3-Butadiene
2-Ethylhexanol
2,4-Dichlorophenoxyacetic Acid (2,4-D)
2,4-Toluene Diisocyanate
Anetic Acid
Acetic Anhydride
Acetone
Acetylene
Acrylonitrile
Adipic Acid
Aluminum Chloride
Aluminum Hydroxide
Aluminum Sulfate
Aminocarb Pesticide (Matacil)
Ammonia
Ammonium Chloride
Ammonium Nitrate
Ammonium Phosphates
Ammonium Sulfate
Arsine
Barium Sulfate
Benzene
Benzoic Acid
Borax
Boric Acid
Butanols
Butylene
Butyraldehydes
Calcium Carbide
Calcium Carbonate
Calcium Chloride
Calcium Hypochlorite
Calcium Oxide/Hydroxide
Calcium Phosphate
Caprolactam
Carbaryl
Carbofuran Pesticides
Carbon Dioxide
Carbon Disulfide
Carbon Tetrachloride
Chlordane
Chlorine
Chloroform
Copper Sulfate
Cresols
Cyclohexane
Dicamba
Dichlorobenzene
Dimethyl Ether
Dimethyl Terephthalate
Dinoseb
Diphenylmethane-4,4'-Diisocyanate
Ethanol
Ethanolamine
Ethylbenzene
Ethylene Dibromide
Ethylene Dichloride
Ethylene Glycol
Ethylene Oxide
Ethylene
Fenitrothion
Ferric Chloride
Fluorochloromethanes
Formaldehyde
Formic Acid
Isopropanol
Isopropylbenzene
Latex
Lead Chromate
Lead Oxide
Magnesium Hydroxide
Malathion
Maleic Anhydride
MCPA
Mercury
Methanol
Methyl Methacrylate
Methyl Ethyl Ketone
Methyl Isobutyl Ketone
Methylamines
Methylene Chloride
Morpholine
n-Hexane
Naphtha
Natural Gas
Nitric Acid
Nitrilotriacetic Acid
Nitroglycerine
Nonyl Phenol
PCBs
Pentachlorophenol
Perchloroethylene
Phenol
Phosphoric Acid
Phosphorus
Phthalic Anhydride
Potash (Potassium Chloride)
Potassium Hydroxide
Potassium Sulfate
Propylene Glycols
Propylene Oxide
Propylene
Sodium Aluminate
Sodium Arsenite
Sodium Borohydride
Sodium Carbonate
Sodium Chlorate
Sodium Chloride
Sodium Cyanide
Sodium Dichloroisocyanurate
Sodium Dichromate
Sodium Hydroxide
Sodium Hydrosulfide (Dithionite)
Sodium Hypochlorite
Sodium Phosphates
Sodium Silicates
Sodium Sulfate
Sodium Sulfite
Styrene (Monomer)
Sulfur
Sulfur Dioxide
Sulfuric Acid (and Oleum)
Sulfuryl Chloride
Tall Oil
Terephthalic Acid
Terphenyls
Tetraethyl Lead
Titanium Dioxide
Toluene
Triallate Pesticides
Trichlorofon Pesticides

Hydrazine
Hydrogen
Hydrogen Chloride/Acid
Hydrogen Fluoride/Acid
Hydrogen Peroxide
Hydrogen Sulfide
Trifluralin Pesticides
Trinitrotoluene
Turpentine
Urea
Vinyl Acetate
Vinyl Chloride
Yellow Cake
Xylenes
Zinc Chloride
Zinc Sulfide
Zinc Oxide

DEVELOPMENT OF A NEW PRIORITY LIST

There are a number of motivations to developing a new priority list:

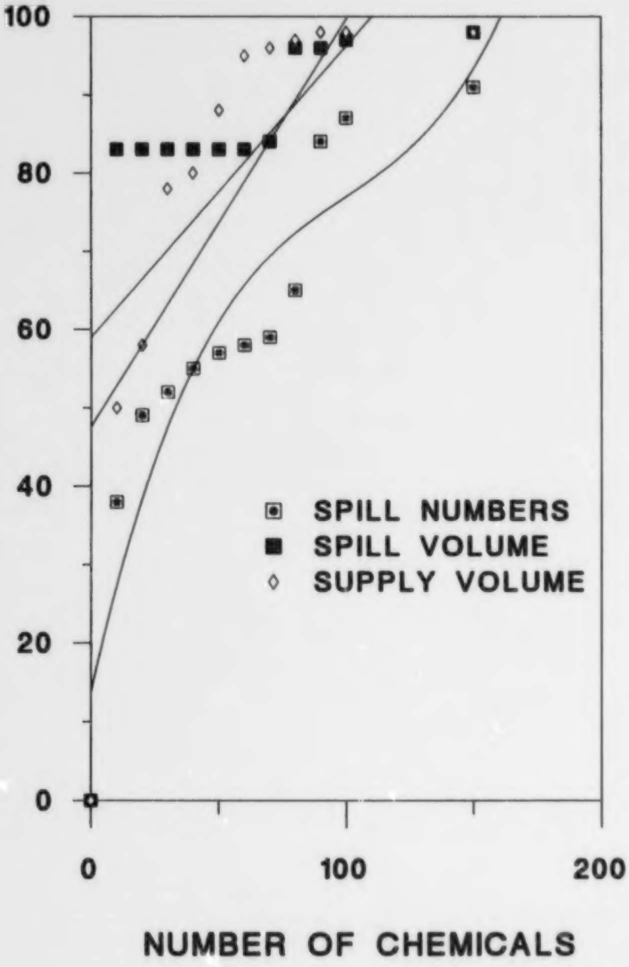
1. The spill history used for the first priority list was weak, with only 2 years of "good" data,
2. There may be a change in spill statistics due to a change in chemical use and transportation patterns,
3. In the first list, the use of toxicity information was weak, resulting in rather innocuous substances appearing high on the priority list,
4. The quantity of aquatic toxicity information has increased and this could be used as a separate consideration as "environmental" toxicity,
5. Although the earlier priority list was useful and had a high utility, there were some notable weaknesses such as the placement of PCBs above the top 50 line,
6. The availability of modern computer tools would enable a rapid and thorough re-evaluation, and
7. Ten years is an appropriate time to re-evaluate the list.

The objectives and principles for the new list development were set as the following:

1. The list should be developed in a systematic and mechanical fashion- that is the placement of individual compounds will only be due to the algorithm used and not on the basis of human judgement,
2. The high volume and frequently spilled chemicals should appear at the top of the list, but toxicity should affect their relative placement,
3. Toxicity will be divided into two considerations, mammalian and aquatic, encompassing both environmental and health concerns,
4. As in the first list, one of the prime objectives is to produce a list that contains as few chemicals as possible to deal with the largest number and volume of spills,
5. All possible candidates will be evaluated (only about 250 were considered in 1980),
6. Completely innocuous materials will be removed from consideration to ensure that they do not appear in any final priority lists, and
7. Several sizes of groupings (eg. 10, 25, 50, etc.) will be prepared to allow use for a variety of purposes.

UTILITY OF THE 1980 PRIORITY LIST

FIGURE 1
PERCENTAGE ACCOUNTED FOR



The procedure employed for developing the new list is outlined in Figure 2. Candidate chemicals and hazardous substances other than oil, were taken from all known spill priority lists such as those published by the United States Environmental Protection Agency, The American Association of Rail Roads and The United States Coast Guard. Lists of materials from the Transport of Dangerous Goods Act were also included. The United States Environmental Protection Agency has published a "List of Lists" which includes substances noted in RCRA, SARA and CERCLA legislation. References 4 to 13 provide details on these. Most of these lists are also summarized in the Appendix, Table A4, "List Membership Comparison".

After the potential candidates were accumulated, they were reviewed for synonyms and substances that were just different forms of each other. This reduced the list by about 5%. All chemicals on the list were reviewed for toxicity and other forms of hazards such as flammability or explosiveness. Substances that showed no danger were removed. Similarly those substances that were human foods or drugs were also removed. These processes reduced the list by a further 10%.

Data on aquatic and mammalian toxicity were collected from standard reference sources. Aquatic data included the results of acute lethal toxicity testing on Rainbow Trout, Blue Gill, Fathead minnow and to Daphnia Magna. Aquatic data on similar species was collected if none of the above were available. Data was found for over 50% of the named compounds. Oral and inhalation toxicity to the rat were collected for the mammalian toxicity along with some human data. Data were available for over 90% of substances on the list.

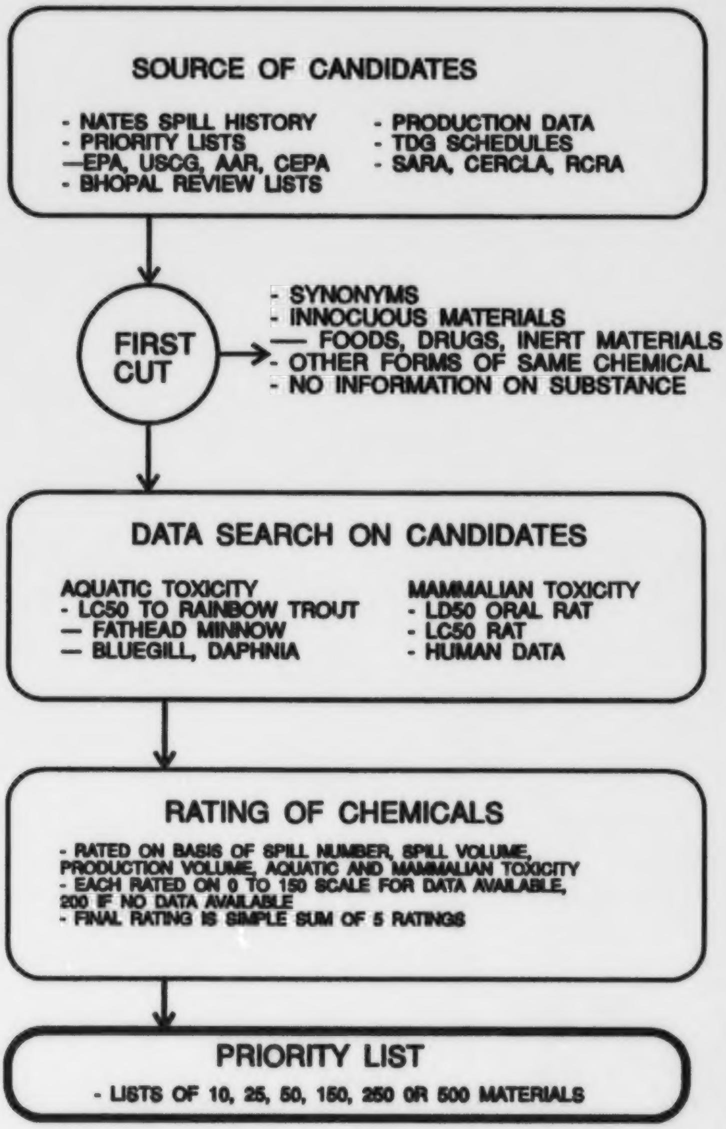
To rank all the toxicity data for the final priority, the lowest typical value for aquatic and the lowest typical mammalian oral toxicity was assigned the value of 1 and the highest, the value of 150. Substances with no data were rated 200.

Similarly, the spill numbers, volume and supply volume of the chemicals were ranked between 1 and 150. Substances with no spill history or commerce data were rated 200. The sum of the ranking for each of the five categories (spill numbers, spill volume, supply volume, aquatic toxicity and mammalian toxicity) were simply added to yield an overall value. These overall values are then directly related to the order of priority, lowest number first. The top priority chemicals are listed in Table 3.

The utility of this new list was analyzed like the 1980 list and a graph of this is shown in Figure 3. The first 10 priority substances account for 43% of spill numbers, 25% of spill volume and 15% of supply volume. The first 50 substances account for 80% of spill numbers, 97% of spill volume and 65% of supply volume. The 150 top priority chemicals account for 97% of spill numbers, 98% of spill

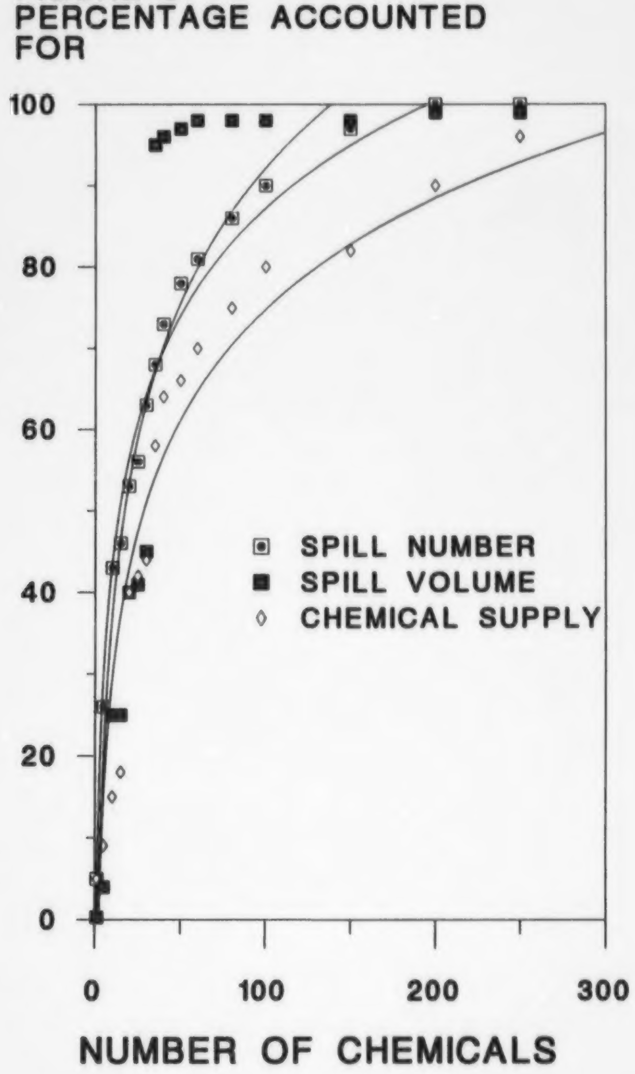
SUMMARY PROCESS FOR DEVELOPMENT OF REVISED PRIORITY LIST

FIGURE 2


SOURCE OF CANDIDATES
- NATES SPILL HISTORY
- PRIORITY LISTS
—EPA, USCG, AAR, CEPA
- BHOPAL REVIEW LISTS
- PRODUCTION DATA
- TDG SCHEDULES
- SARA, CERCLA, RCRA
FIRST CUT
- SYNONYMS
- INNOCUOUS MATERIALS
— FOODS, DRUGS, INERT MATERIALS
- OTHER FORMS OF SAME CHEMICAL
- NO INFORMATION ON SUBSTANCE
DATA SEARCH ON CANDIDATES
AQUATIC TOXICITY
- LC50 TO RAINBOW TROUT
— FATHEAD MINNOW
— BLUEGILL, DAPHNIA
MAMMALIAN TOXICITY
- LD50 ORAL RAT
- LC50 RAT
- HUMAN DATA
RATING OF CHEMICALS
- RATED ON BASIS OF SPILL NUMBER, SPILL VOLUME, PRODUCTION VOLUME, AQUATIC AND MAMMALIAN TOXICITY
- EACH RATED ON 0 TO 150 SCALE FOR DATA AVAILABLE, 200 IF NO DATA AVAILABLE
- FINAL RATING IS SIMPLE SUM OF 5 RATINGS
PRIORITY LIST
- LISTS OF 10, 25, 50, 150, 250 OR 500 MATERIALS

UTILITY OF PRIORITY LIST

FIGURE 3



volume and 82% of supply volume. This utility is much higher than the previous priority list and easily satisfies the starting criteria.

Analysis of the priority lists shows that the differences between the old and new lists are not major. Only 14 of the top 50 are different, and the 14 fall in the next 150 priority materials. Order is somewhat different and the list achieves the goal of having higher toxicity materials appear at a higher priority level.

Because of the restrictions on paper size for this conference. Full data tables will not be given. Basic data is found in the Appendix.

REFERENCES

1. Beach, R.A., "Information Systems Used in Environmental Emergencies", Spill Technology Newsletter, V.3, No. 5, pp. 283-287, 1978.

2. Fingas, M.F, "The Development of Improved Countermeasures for Chemical Spills in Canada", Proceedings of the 1984 Hazardous Materials Conference, Hazardous Material Institutes, Rockville, Maryland, pp. 255-260, 1984.

3. Fingas, M., Papers, Tables and Other Data Relating to the Development of a Chemical Spill Priority List for the Environmental Protection Service, Environmental Emergencies Technology Division, Environment Canada, Ottawa, 1984.

4. U.S. Coast Guard, Chemical Hazards Response Information System, Manual 2, 1978.

5. U.S. Environmental Protection Agency, Federal Register, 44, No. 128, 38746-38776, 1979.

6. Hobbs, John R., Monitoring Devices for Railroad Response Teams, U.S. Department of Transport, Cambridge, Ma., 1985.

7. U.S. Environmental Protection Agency, Federal Register, 51, No. 188, 34534-34549, 1986.

8. U.S. Environmental Protection Agency, Hazardous Material Intelligence Report, December 1985.

9. "Regulations respecting the handling, offering for transport, and transporting of dangerous goods", Canada Gazette, 1985.

10. U.S. Environmental Protection Agency, Toxic Substances Control Act Chemical Substances Inventory, Cumulative Supplement II, 1982.

11. U.S. Environmental Protection Agency, Perspectives on the Top 50 Production Volume Chemicals, 1980.

12. Association of American Railroads, The AAR Hazardous Materials Data Base, Part I and II, 1981.

13. U.S. Environmental Protection Agency, List of lists, July 1987.

TABLE 3 THE 1990 CHEMICAL SPILL PRIORITY LIST

THE TOP TEN MATERIALS

- Ammonia
- Chlorine
- Hydrochloric acid
- PCBs
- Pentachlorophenol
- Potassium chloride
- Sodium cyanide
- Styrene
- Sulfuric acid
- Tetraethyl lead

THE TOP TWENTY FIVE MATERIALS

- Ammonia
- Ammonium hydroxide
- Ammonium sulfate
- Benzene
- Calcium chloride
- Calcium hypochlorite
- Chlorine
- Copper sulfate
- Formaldehyde
- Hydrochloric acid
- PCBs
- Pentachlorophenol
- Phenol
- Phosphorus
- Potassium chloride
- Sodium chlorate
- Sodium chloride
- Sodium cyanide
- Sodium hydroxide
- Styrene
- Sulfuric acid
- Tetraethyl lead
- Toluene
- Xylene
- Zinc sulfate

THE TOP 50 MATERIALS

- Acetic acid
- Aldrin
- Aminocarb
- Ammonia
- Ammonium hydroxide
- Ammonium nitrate
- Ammonium phosphates
- Ammonium sulfate
- Benzene
- Calcium chloride
- Calcium hydroxide
- Calcium hypochlorite
- Carbon tetrachloride
- Chlorine
- Copper sulfate
- Ethylbenzene
- Ethylene dichloride
- Ethylene glycol
- Ethylhexanol
- Fenitrothion
- Ferric chloride
- Formaldehyde
- Hydrochloric acid
- Methyl alcohol
- Nitric acid
- Nonylphenol
- PCBs
- Pentachlorophenol
- Perchloroethylene
- Phenol
- Phosphamidon
- Phosphoric acid
- Phosphorus
- Potassium chloride
- Propylene oxide
- Sodium carbonate
- Sodium chlorate
- Sodium chloride
- Sodium cyanide
- Sodium hydroxide
- Styrene
- Sulfur
- Sulfur dioxide
- Sulfuric acid
- Tetraethyl lead
- Toluene
- Vinyl acetate
- Xylene
- Zinc sulfate
- 2,4-dichlorophenoxyacetic acid (2,4-D)

APPENDIX

TABLE A1 LISTS OF THE TOP 10,25,50,150 AND 250 PRIORITY SPILL MATERIALS

TABLE A2 LIST OF THE TOP 500 PRIORITY CHEMICALS

TABLE A3 ANALYSIS OF THE TOP 500 CHEMICALS

TABLE A4 LIST MEMBERSHIP COMPARISON

TABLE A5 AQUATIC TOXICITY GATHERED ON THE CHEMICALS

TABLE A6 MAMMALIAN TOXICITY GATHERED ON THE CHEMICALS

TABLE A1 THE 1990 CHEMICAL SPILL PRIORITY LIST

THE TOP TEN MATERIALS

Ammonia
Chlorine
Hydrochloric acid
PCBs
Pentachlorophenol
Potassium chloride
Sodium cyanide
Styrene
Sulfuric acid
Tetraethyl lead

THE TOP TWENTY FIVE MATERIALS

Ammonia
Ammonium hydroxide
Ammonium sulfate
Benzene
Calcium chloride
Calcium hypochlorite
Chlorine
Copper sulfate
Formaldehyde
Hydrochloric acid
PCBs
Pentachlorophenol
Phenol
Phosphorus
Potassium chloride
Sodium chlorate
Sodium chloride
Sodium cyanide
Sodium hydroxide
Styrene
Sulfuric acid
Tetraethyl lead
Toluene
Xylene
Zinc sulfate

THE TOP 50 MATERIALS

Acetic acid
Aldrin
Aminocarb
Ammonia
Ammonium hydroxide
Ammonium nitrate
Ammonium phosphates
Ammonium sulfate
Benzene
Calcium chloride
Calcium hydroxide
Calcium hypochlorite
Carbon tetrachloride
Chlorine
Copper sulfate
Ethylbenzene
Ethylene dichloride
Ethylene glycol
Ethylhexanol
Fenitrothion
Ferric chloride
Formaldehyde
Hydrochloric acid
Methyl alcohol
Nitric acid
Nonylphenol
PCBs
Pentachlorophenol
Perchloroethylene
Phenol
Phosphamidon
Phosphoric acid
Phosphorus
Potassium chloride
Propylene oxide
Sodium carbonate
Sodium chlorate
Sodium chloride
Sodium cyanide
Sodium hydroxide
Styrene
Sulfur
Sulfur dioxide
Sulfuric acid
Tetraethyl lead
Toluene
Vinyl acetate
Xylene
Zinc sulfate
2,4-dichlorophenoxyacetic acid (2,4-D)

LIST OF THE TOP 150 MATERIALS

Acetic acid
Acetic anhydride
Acetone
Acetylene
Acrylonitrile
Aldrin
Aluminum sulfate
Aminocarb
Ammonia
Ammonium chloride
Ammonium hydroxide
Ammonium nitrate
Ammonium phosphates
Ammonium sulfate
Aniline
Atrazine
Azinphosmethyl
Benzene
Benzene hexachloride (Lindane)
Benzoic acid
Benzotrifluoride
Bromoform
Butyl alcohol
Calcium chloride
Calcium cyanide
Calcium hydroxide
Calcium hypochlorite
Calcium oxide
Calcium phosphate
Carbaryl
Carbofuran
Carbon tetrachloride
Chlordane
Chlorine
Chlorophenol
Chromic acid
Cobaltous nitrate
Copper cyanide
Copper sulfate
Cresol
Cyclohexane
Diazinon
Dicamba
Maneb
MCPA
Mercury
Methoxychlor
Methyl alcohol
Methyl chloride
Methyl ethyl ketone
Methyl methacrylate
Methylamine
Methylene chloride
Naphthalene
Nitric acid
Nitroaniline
Nitrogen (liquefied)
Nonylphenol
Oxygen (liquefied)
Paraquat
Parathion
PCBs
Pentachlorophenol
Perchloroethylene
Phenol
Phosphamidon
Phosphoric acid
Phosphorus
Phthalic anhydride
Picloram
Potassium chloride
Potassium cyanide
Potassium hydroxide
Potassium permanganate
Propionic acid
Propylene
Propylene glycol
Propylene oxide
Pyridine
Sodium carbonate
Sodium chlorate
Sodium chloride
Sodium cyanide
Sodium fluoride
Sodium hydrosulfite
Sodium hydroxide

LIST OF THE TOP 150 MATERIALS ctd.

Dichlorvos
Dieldrin
Diethanolamine
Diethylamine
Dimethylamine
Dinitramine
Dinoseb
Diphenyl ether
Diquat
Endrin
Ethyl alcohol
Ethyl chloride
Ethylbenzene
Ethylene
Ethylene dichloride
Ethylene glycol
Ethylene oxide
Ethylhexanol
Fenitrothion
Ferric chloride
Formaldehyde
Formic acid
Hexane
Hydrazine
Hydrochloric acid
Hydrofluoric acid
Hydrogen peroxide
Isopropyl alcohol
Lead oxide
Lignin sulfonate
Malathion
Maleic anhydride
Sodium hypochlorite
Sodium silicate
Sodium sulfite
Styrene
Sulfur
Sulfur dioxide
Sulfuric acid
Terephthalic acid
Tetraethyl lead
Thallium sulfate
Thioglycolic acid
Titanium dioxide
Toluene
Toluene-2,4-diamine
Toluene-2,4-diisocyanate
Tributyl phosphate
Trichloroethane
Trichloroethylene
Trichlorofon
Trifluralin
Trinitrotoluene
Uranyl nitrate
Vinyl acetate
Vinyl chloride
Xylene
Zinc chloride
Zinc cyanide
Zinc oxide
Zinc phosphate
Zinc sulfate
2,4,5-Trichlorophenoxyacetic . (2,4,5-T)
2,4-dichlorophenoxyacetic acid (2,4-D)

LIST OF THE TOP 250 MATERIALS

Acetaldehyde
Acetic acid
Acetic anhydride
Acetone
Acetone cyanohydrin
Acetylene
Acrolein
Acrylamide
Acrylonitrile
Aldicarb
Aldrin
Allyl alcohol
Aluminum chloride
Aluminum sulfate
Aminocarb
Ammonia
Ammonium chloride
Ammonium hydroxide
Ammonium nitrate
Ammonium phosphates
Ammonium sulfate
Aniline
Antimony trioxide
Arsenic acid
Arsine
Asbestos
Atrazine
Azinphos ethyl
Azinphosmethyl
Barium sulfate
Benzene
Benzene hexachloride (Lindane)
Benzoic acid
Benzotrifluoride
Borax
Bromoform
Brucine
Butyl alcohol
Butyl formate
Cadmium
Cadmium sulfate
Calcium arsenate
Calcium carbide
Calcium chloride
Calcium cyanide
Calcium hydroxide
Hydrochloric acid
Hydrocyanic acid
Hydrofluoric acid
Hydrogen peroxide
Hydrogen sulfide
Hydroquinone
Isodrin
Isopropyl alcohol
Kepone
Lead oxide
Lignin sulfonate
Magnesium hydroxide
Malathion
Maleic anhydride
Maneb
MCPA
Mercuric acetate
Mercuric chloride
Mercuric thiocyanate
Mercurous nitrate
Mercury
Methiocarb
Methoxychlor
Methoxyethylmercuric acetate
Methyl alcohol
Methyl chloride
Methyl ethyl ketone
Methyl methacrylate
Methyl parathion
Methylamine
Methylene chloride
Mevinphos
Naled
Naphthalene
Nickel carbonyl
Nitric acid
Nitroaniline
Nitrogen (liquefied)
Nitrogen dioxide
Nitrous oxide
Nonylphenol
Oxygen (liquefied)
Paraquat
Parathion
PCBs
Pentachlorophenol

LIST OF THE TOP 250 MATERIALS ctd.

Calcium hypochlorite
Calcium nitrate
Calcium oxide
Calcium phosphate
Carbaryl
Carbofuran
Carbon dioxide
Carbon disulfide
Carbon tetrachloride
Cesium 137
Chlordane
Chlorine
Chlorine dioxide
Chloroaniline
Chloroform
Chlorohydrin
Chlorophenol
Chlorpyrifos
Chromic acid
Cobaltous nitrate
Copper chloride
Copper cyanide
Copper sulfate
Coumaphos
Cresol
Cumene
Cyanogen bromide
Cyclohexane
Cycloheximide
Cyclohexylamine
DDT
Demeton
Diallate
Diazinon
Dicamba
Dichlone
Dichlorvos
Dicrotophos
Dieldrin
Diethanolamine
Diethylamine
Dimethylamine
Dinitramine
Dinitrocresols
Dinoseb
Perchloroethylene
Phenol
Phenolsulfonic acid
Phenyl mercuric acetate
Phosphamidon
Phosphoric acid
Phosphorus
Phosphorus pentoxide
Phthalic anhydride
Picloram
Potassium carbonate
Potassium chloride
Potassium cyanide
Potassium hydroxide
Potassium permanganate
Propargyl alcohol
Propionic acid
Propylene
Propylene glycol
Propylene oxide
Pyridine
Rotenone
Sodium aluminate
Sodium arsenite
Sodium azide
Sodium borohydride
Sodium carbonate
Sodium chlorate
Sodium chloride
Sodium chromate
Sodium cyanide
Sodium dichromate
Sodium fluoride
Sodium hydrosulfite
Sodium hydroxide
Sodium hypochlorite
Sodium nitrate
Sodium phosphate
Sodium silicate
Sodium sulfite
Strychnine
Styrene
Sulfur
Sulfur dioxide
Sulfuric acid

LIST OF THE TOP 250 MATERIALS ctd.

Dioxathion
Diphenyl
Diphenyl ether
Diquat
Disulfoton
Endosulfan
Endothall
Endrin
Ethion
Ethyl acrylate
Ethyl alcohol
Ethyl chloride
Ethyl mercaptan
Ethylamine
Ethylbenzene
Ethylene
Ethylene dichloride
Ethylene glycol
Ethylene oxide
Ethylhexanol
Fenitrothion
Ferric chloride
Ferric oxide
Ferrous sulfate
Flamprop-methyl
Fonofos
Formaldehyde
Formic acid
Glyphosate
Heavy water
Hexachlorobutadiene
Hexachlorophene
Hexane
Hydrazine
Terephthalic acid
Tetraethyl lead
Tetraethyl pyrophosphate
Thallium sulfate
Thioglycolic acid
Thiram
Titanium dioxide
Toluene
Toluene-2,4-diamine
Toluene-2,4-diisocyanate
Toxaphene
Tributyl phosphate
Trichloroethane
Trichloroethylene
Trichlorofon
Triethanolamine
Trifluralin
Trimethylene bromide
Trinitrotoluene
Uranyl nitrate
Urea
Vanadium pentoxide
Vinyl acetate
Vinyl chloride
Xylene
Zinc chloride
Zinc cyanide
Zinc oxide
Zinc phosphate
Zinc sulfate
2,3,4,6-Tetrachlorophenol
2,4,5-Trichlorophenoxyacetic .(2,4,5-T)
2,4-dichlorophenoxyacetic acid (2,4-D)
2,4-Dinitrophenol

THE TOP FIVE HUNDRED PRIORITY MATERIALS

Acetaldehyde
Acetic acid
Acetic anhydride
Acetone
Acetone cyanohydrin
Acetophenone
Acetyl chloride
Acetylene
Acrolein
Acrylamide
Acrylonitrile
Adipic acid
Adiponitrile
Alachlor
Aldicarb
Aldrin
Allyl alcohol
Allyl chloride
Aluminum chloride
Aluminum phosphate
Aluminum sulfate
Aminocarb
Amiton
Ammonia
Ammonium chloride
Ammonium hydroxide
Ammonium nitrate
Ammonium phosphates
Ammonium picrate
Ammonium stearate
Ammonium sulfamate
Ammonium sulfate
Aniline
Anthracene
Antimony trioxide
Arsenic
Arsenic acid
Arsenic pentoxide
Arsenic trioxide
Arsine
Asbestos
Atlox
Atrazine
Azinphos ethyl
Azinphosmethyl
Barban
Barium sulfate
Benzaldehyde
Benzene
Benzene hexachloride (Lindane)
Benzidine
Benzoic acid
Benzonitrile
Benzophenone
Benzotrifluoride
Benzoyl chloride
Benzyl alcohol
Benzyl chloride
Benzyl-n-butyl phthalate
Beryllium
Bisphenol A
Borax
Boric acid
Bromine
Bromoform
Brucine
Butadiene
Butyl alcohol
Butyl formate
Butyl mercaptan
Butylamine
Butylene
Butyraldehyde
Butyric acid
Cadmium
Cadmium chloride
Cadmium nitrate
Cadmium sulfate
Calcium arsenate
Calcium carbide
Calcium carbonate
Calcium chloride
Calcium cyanide
Calcium fluoride
Calcium hydroxide
Calcium hypochlorite
Calcium nitrate
Calcium oxide
Calcium phosphate
Camphor oil
Cantharidin
Caprolactam
Carbaryl
Carbofuran
Carbon dioxide
Carbon disulfide

THE TOP FIVE HUNDRED PRIORITY MATERIALS ctd.

Carbon tetrachloride
Carbonyl sulfide
Carboxymethylcellulose
Cesium 137
Chlordane
Chlorine
Chlorine dioxide
Chloroaniline
Chlorobenzene
Chlorodifluoromethane
Chloroethylvinyl ether
Chloroform
Chlorohydrin
Chlorophacinone
Chlorophenol
Chloroxuron
Chlorpropham
Chlorpyrifos
Choline chloride
Chromic acid
Chromic sulfate
Chromium
Chromous chloride
Cobaltous bromide
Cobaltous chloride
Cobaltous hydroxide
Cobaltous nitrate
Copper acetate
Copper chloride
Copper cyanide
Copper nitrate
Copper sulfate
Coumaphos
Cresol
Crimidine
Crotonaldehyde
Cumene
Cyanogen bromide
Cyclohexane
Cyclohexanone
Cycloheximide
Cyclohexylamine
Dalapon
DDT
Decyl alcohol
Decyl octyl phthalate
Demeton
Diallate
Diazinon
Dibromomethane
Dibutyl amine
Dibutyl ether
Dicamba
Dichlobenil
Dichlone
Dichlorodifluoromethane
Dichloroethyl amino uracil
Dichloroethyl ether
Dichlorvos
Dicrotophos
Dieldrin
Diethanolamine
Diethyl chlorophosphate
Diethyl phthalate
Diethyl-m-toluamide
Diethyl-p-nitrophenyl phosphate
Diethylamine
Diisopropylamine
Dimefox
Dimethoate
Dimethyl ethyl amine
Dimethyl phthalate
Dimethyl sulfate
Dimethylamine
Dimethylaniline
Dinitramine
Dinitroaniline
Dinitrobenzene
Dinitrocresols
Dinoseb
Dioxathion
Diphacinone
Diphenyl
Diphenyl ether
Diphenylamine
Diphenylmethane-4,4'-diisocyanate
Diquat
Disulfoton
Dithiobiuret
Diuron
Dodecylbenzenesulfonic acid
Endosulfan
Endothall
Endrin
Epichlorohydrin

THE TOP FIVE HUNDRED PRIORITY MATERIALS ctd.

EPN
Eptam
Ethanolamine
Ethion
Ethyl acetate
Ethyl acrylate
Ethyl alcohol
Ethyl chloride
Ethyl mercaptan
Ethylamine
Ethylbenzene
Ethylene
Ethylene dibromide
Ethylene dichloride
Ethylene glycol
Ethylene glycol monobutyl ether
Ethylene oxide
Ethylene thiourea
Ethyleneimine
Ethylhexanol
Fenitrothion
Fensulfothion
Ferric chloride
Ferric hydroxide
Ferric oxide
Ferrous sulfate
Flamprop-methyl
Fluenetil
Fluometuron
Fluoranthene
Fluorine
Fluoroacetamide
Fluoroacetic acid
Fonofos
Formaldehyde
Formic acid
Fumaric acid
Furazolidone
Furfural
Furfuryl alcohol
Glycerine
Glycidyl methacrylate
Glyphosate
Heavy water
Heptanol
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Hexachlorophene
Hexaethyl tetraphosphate
Hexaldehyde
Hexane
Hexanol
Hydrazine
Hydrochloric acid
Hydrocyanic acid
Hydrofluoric acid
Hydrogen
Hydrogen peroxide
Hydrogen sulfide
Hydroquinone
Iodomethane
Isobenzan
Isobutyl acrylate
Isobutyl alcohol
Isodrin
Isooctyl alcohol
Isophorone
Isopropyl alcohol
Isopropylmethylpyrazolyl dimet.car.
Isovaleraldehyde
Kepone
Lactonitrile
Lead arsenate
Lead chloride
Lead fluoroborate
Lead oxide
Lignin sulfonate
Lithium bromide
Magnesium hydroxide
Magnesium oxide
Malathion
Maleic acid
Maleic anhydride
Malononitrile
Maneb
MCPA
Melamine
Mephosfolan
Mercuric acetate
Mercuric chloride
Mercuric sulfide
Mercuric thiocyanate
Mercurous nitrate
Mercury

THE TOP FIVE HUNDRED PRIORITY MATERIALS ctd.

- Methanesulfonyl fluoride
- Methiocarb
- Methoxychlor
- Methoxyethylmercuric acetate
- Methyl alcohol
- Methyl amyl alcohol
- Methyl bromide
- Methyl chloride
- Methyl ethyl ketone
- Methyl ethyl ketone peroxide
- Methyl hexyl ketone
- Methyl isobutyl ketone
- Methyl methacrylate
- Methyl parathion
- Methyl phenkapton
- Methylamine
- Methylene chloride
- Methylstyrene
- Metobromuron
- Mevinphos
- Mexacarbate
- Monocrotophos
- Morpholine
- N,N-Dimethylaniline
- N-Nitrosodiphenylamine
- Naled
- Naphtha
- Naphthalene
- Naphthol
- Neopentyl glycol
- Nickel carbonyl
- Nickel chloride
- Nicotine sulfate
- Nitralin
- Nitric acid
- Nitrilotriacetic acid
- Nitroaniline
- Nitrobenzene
- Nitrogen (liquefied)
- Nitrogen dioxide
- Nitroglycerin
- Nitromethane
- Nitrophenol
- Nitropropane
- Nitrosodimethylamine
- Nitrotoluene
- Nitrous oxide
- Nonane
- Nonanol
- Nonylphenol
- Octanol
- Oleic acid
- Oleum
- Oxalic acid
- Oxygen (liquefied)
- Paraquat
- Parathion
- PCBs
- Pentachlorobenzene
- Pentachlorophenol
- Perchloroethylene
- Phenanthrene
- Phenol
- Phenolsulfonic acid
- Phenyl mercuric acetate
- Phenylenediamine
- Phenylthiourea
- Phorate
- Phosgene
- Phosmet
- Phosphamidon
- Phosphine
- Phosphoric acid
- Phosphorus
- Phosphorus pentoxide
- Phthalic anhydride
- Picloram
- Potassium aluminate
- Potassium carbonate
- Potassium chlorate
- Potassium chloride
- Potassium cyanide
- Potassium dichromate
- Potassium hydroxide
- Potassium permanganate
- Potassium sulfate
- Propargyl alcohol
- Propionaldehyde
- Propionic acid
- Propionic anhydride
- Propylamine
- Propylene
- Propylene chlorohydrin
- Propylene glycol
- Propylene oxide
- Pyridine

THE TOP FIVE HUNDRED PRIORITY MATERIALS ctd.

Pyrocatechol
Quinoline
Quinone
Resorcinol
Rotenone
Salicylic acid
Silver nitrate
Sodium
Sodium aluminate
Sodium anthraquinone sulfate
Sodium arsenate
Sodium arsenite
Sodium azide
Sodium bisulfite
Sodium borohydride
Sodium carbonate
Sodium chlorate
Sodium chloride
Sodium chromate
Sodium cyanide
Sodium dichromate
Sodium fluoride
Sodium fluoroacetate
Sodium fluorosilicate
Sodium hydrosulfide
Sodium hydrosulfite
Sodium hydroxide
Sodium hypochlorite
Sodium nitrate
Sodium nitrilotriacetic acid
Sodium phosphate
Sodium phosphate, tribasic
Sodium selenite
Sodium silicate
Sodium sulfate
Sodium sulfite
Sodium thioglycolate
Stannic chloride
Stannous chloride
Strychnine
Strychnine sulfate
Styrene
Sulfamic acid
Sulfotepp
Sulfur
Sulfur chloride
Sulfur dioxide
Sulfuric acid
Sulfuryl chloride
Temephos
Terephthalic acid
Terphenyl
Tetraethyl lead
Tetraethyl pyrophosphate
Tetrahydronaphthalene
Tetramethyl lead
Thallium
Thallium acetate
Thallium sulfate
Thioglycolic acid
Thionyl chloride
Thiosemicarbazide
Thiourea
Thiram
Titanium dioxide
Toluene
Toluene-2,4-diamine
Toluene-2,4-diisocyanate
Toluidine
Toxaphene
Tributyl phosphate
Trichlorobenzene
Trichloroethane
Trichloroethylene
Trichlorofon
Trichlorophenol
Trichlorophenoxy propionic acid
Tridecyl alcohol
Triethanolamine
Triethylamine
Trifluralin
Trimethylamine
Trimethylene bromide
Trinitrotoluene
Turpentine
Uranyl nitrate
Urea
Valeraldehyde
Vanadium pentoxide
Vinyl acetate
Vinyl chloride
Warfarin
Xylene
Xylenol
Yellow cake

THE TOP FIVE HUNDRED PRIORITY MATERIALS ctd.

Zinc acetate
Zinc bromide
Zinc chloride
Zinc cyanide
Zinc oxide
Zinc phosphate
Zinc sulfate
1,1-Dichloropropane
1,2,4,5-Tetrachlorobenzene
2,2'-Thiobis(4,6-dichlorophenol)
2,3,4,6-Tetrachlorophenol
2,3-Dibromo-1-propanol phosphate
2,4,5-Trichlorophenoxyacetic . (2,4,5-T)
2,4-Dichlorophenol
2,4-dichlorophenoxyacetic acid (2,4-D)
2,4-Dinitrophenol
2,4-Dinitrotoluene
2-Phenylphenol
4-Aminopyridine
5-[Bis(2-chloroethyl)amino] uracil

[illegible]		SPILL	SPILL	SUPPLY	%	%	%
CHEMICAL	RANK	NUMBER	VOLUME	VOLUME	NUMBER	VOLUME	SUPPLY
Ammonia	1	107	470	3700	5.5	0.3	5.5
Chlorine	2	36	120	1700	7.3	0.4	8
Tetraethyl lead	3	4	72	26	7.5	0.5	8
Styrene	4	24	5000	630	8.7	4.1	8.9
PCBs	5	334	89		25.9	4.2	8.9
Sulfuric acid	6	155	13000	3700	33.9	13.6	14.4
Sodium cyanide	7	3	83	12	34.1	13.7	14.4
Hydrochloric acid	8	123	3300	170	40.4	16.1	14.7
Potassium chloride	9	31	12000		42	24.8	14.7
Pentachlorophenol	10	19	110	1.5	43	24.9	14.7
Phenol	11	10	14	68	43.5	24.9	14.8
Zinc sulfate	12	3	66	1500	43.7	24.9	17
Phosphorus	13	16	46	68	44.5	24.9	17.1
Toluene	14	13	110	430	45.2	25	17.7
Copper sulfate	15	5	23	24	45.5	25	17.7
Sodium chloride	16	12	1400	12000	46.1	26	35.6
Calcium chloride	17	20	3700	340	47.1	28.7	36.1
Sodium hydroxide	18	92	8200	1800	51.8	34.6	38.8
Sodium chlorate	19	23	7700	440	53	40.2	39.5
Ammonium sulfate	20	8	260	330	53.4	40.4	40
Ammonium hydroxide	21	15	130		54.2	40.5	40
Benzene	22	12	14	740	54.8	40.5	41.1
Xylene	23	14	47	290	55.5	40.5	41.5
Calcium hypochlorite	24	4	17	7.9	55.7	40.5	41.5
Formaldehyde	25	10	41	130	56.2	40.5	41.7
Acetic acid	26	9	73	71	56.7	40.6	41.8
Methyl alcohol	27	18	740		57.6	41.1	41.8
2,4-dichlorophenoxyacetic acid (2,4-D)	28	37	130	3	59.5	41.2	41.8
Ethylene dichloride	29	1	780	820	59.6	41.8	43
Ammonium nitrate	30	63	4200	910	62.8	44.8	44.4
Sulfur	31	68	70000	7400	66.3	95.5	55.4
Sodium carbonate	32	3	26	570	66.5	95.5	56.2
Ammonium phosphates	33	5	140	1400	66.8	95.6	58.3
Propylene oxide	34	2	22	61	66.9	95.6	58.4
Perchloroethylene	35	10	15	27	67.4	95.6	58.4
Calcium hydroxide	36	17	360	2600	68.3	95.9	62.3
Nonylphenol	37	2	8.8	7	68.4	95.9	62.3
Ethylbenzene	38	4	0.79	720	68.6	95.9	63.4
Ethylene glycol	39	31	590	410	70.2	96.3	64
Fenitrothion	40	49	100		72.7	96.4	64
Aminocarb	41	12	55		73.3	96.4	64
Carbon tetrachloride	42	1	1.8	26	73.4	96.4	64
Vinyl acetate	43	8	7.4	44	73.8	96.4	64.1
Sulfur dioxide	44	16	90	140	74.6	96.5	64.3
Nitric acid	45	48	140	890	77.1	96.6	65.6
Phosphamidon	46	8	16		77.5	96.6	65.6
Aldrin	47	2	1.3		77.6	96.6	65.6
Phosphoric acid	48	12	37	520	78.2	96.6	66.4
Ferric chloride	49	8	1000		78.6	97.3	66.4
Ethylhexanol	50	1	100		78.7	97.4	66.4
Hydrofluoric acid	51	5	0.68	77	79	97.4	66.5
Toluene-2,4-diisocyanate	52	7	2		79.4	97.4	66.5
Ethyl alcohol	53	3	51		79.6	97.4	66.5
Carbaryl	54	2	70		79.7	97.5	66.5
Parathion	55	1	0.01		79.8	97.5	66.5
Calcium oxide	56	12	530	2600	80.4	97.9	70.4
MCPA	57	5	0.91		80.7	97.9	70.4
Methylene chloride	58	4	6.2	10	80.9	97.9	70.4
Paraquat	59	2	44		81	97.9	70.4
Hydrazine	60	3	4.5		81.2	97.9	70.4
Malathion	61	7	0.29		81.6	97.9	70.4
Sodium silicate	62	1	3.8	120	81.7	97.9	70.6
Acrylonitrile	63	1	4.6	16	81.8	97.9	70.6
Trichloroethane	64	4	0.81		82	97.9	70.6
Hexane	65	5	8		82.3	97.9	70.6
Zinc oxide	66	3	55	47	82.5	97.9	70.7
Isopropyl alcohol	67	4	9		82.7	97.9	70.7
Chlordane	68	2	0.003		82.8	97.9	70.7
Potassium cyanide	69	1	0.006		82.9	97.9	70.7
Potassium permanganate	70	4	9.8		83.1	97.9	70.7
Vinyl chloride	71	31	180	440	84.7	98	71.4
2,4,5-Trichlorophenoxyacetic acid (2,4	72	2	0.24		84.8	98	71.4

TABLE A3 - ANALYSIS		SPILL	SPILL	SUPPLY	%	%	%
CHEMICAL	RANK	NUMBER	VOLUME	VOLUME	NUMBER	VOLUME	SUPPLY
Dimethylamine	73	4	33		85	98	71.4
Methyl methacrylate	74	3	3.4	18	85.2	98	71.4
Dieldrin	75	1	0.004		85.3	98	71.4
Diazinon	76	4	0.3		85.5	98	71.4
Acetone	77	4	9.9	23	85.7	98	71.4
Trichlorofon	78	3	2.6		85.9	98	71.4
Naphthalene	79	3	6.4		86.1	98	71.4
Ethylene	80	2	180	2200	86.2	98.1	74.7
Maleic anhydride	81	1	2.8	15	86.3	98.1	74.7
Dinoseb	82	1	0.91		86.4	98.1	74.7
Calcium cyanide	83	1	0.09		86.5	98.1	74.7
Methyl chloride	84	2	2.5	4.1	86.6	98.1	74.7
Benzoic acid	85	2	34	28	86.7	98.1	74.7
Chromic acid	86	8	8.8	2.8	87.1	98.1	74.7
Mercury	87	11	20		87.7	98.1	74.7
Aniline	88	1	0.1	0.62	87.8	98.1	74.7
Oxygen (liquefied)	89	5	24	2700	88.1	98.1	78.7
Aluminum sulfate	90	9	120	220	88.6	98.2	79
Azinphosmethyl	91	1	0		88.7	98.2	79
Hydrogen peroxide	92	7	0.71	34	89.1	98.2	79.1
Sodium hypochlorite	93	11	58	170	89.7	98.2	79.4
Ammonium chloride	94	1	0.7	2.7	89.8	98.2	79.4
Cresol	95	2	13		89.9	98.2	79.4
Cyclohexane	96	1	0.11	60	90	98.2	79.5
Dichlorvos	97	1	0.1		90.1	98.2	79.5
Calcium phosphate	98	3	100	160	90.3	98.3	79.7
Thallium sulfate	99	1	0.03		90.4	98.3	79.7
Butyl alcohol	100	1	2		90.5	98.3	79.7
Trinitrotoluene	101	1	17		90.6	98.3	79.7
Potassium hydroxide	102	2	1.2	12	90.7	98.3	79.7
Phthalic anhydride	103	3	7.2	34	90.9	98.3	79.8
Benzene hexachloride (Lindane)	104	1	0.0009		91	98.3	79.8
Zinc cyanide	105	1	0.2		91.1	98.3	79.8
Zinc chloride	106	1	13		91.2	98.3	79.8
Acetic anhydride	107	8	1.5		91.6	98.3	79.8
Methyl ethyl ketone	108	4	7.7	12	91.8	98.3	79.8
Pyridine	109	2	0.005		91.9	98.3	79.8
Trichloroethylene	110	1	0.13	3	92	98.3	79.8
Cobaltous nitrate	111	1	0.9		92.1	98.3	79.8
Picloram	112	3	0.53		92.3	98.3	79.8
Diethylamine	113	2	1.8		92.4	98.3	79.8
Trifluralin	114	9	4.6		92.9	98.3	79.8
Dicamba	115	2	0.17		93	98.3	79.8
Atrazine	116	2	0.85		93.1	98.3	79.8
Methoxychlor	117	1	0.05		93.2	98.3	79.8
Nitrogen (liquefied)	118	3	1.8	340	93.4	98.3	80.3
Propylene glycol	119	1	8.3	19	93.5	98.3	80.3
Diquat	120	2	0		93.6	98.3	80.3
Chlorophenol	121	1	0.04		93.7	98.3	80.3
Sodium fluoride	122	1	0.2		93.8	98.3	80.3
Benzotrifluoride	123	1	50		93.9	98.3	80.3
Carbofuran	124	4	0.06		94.1	98.3	80.3
Methylamine	125	1	5.3	6.3	94.2	98.3	80.3
Ethyl chloride	126	2	0.2	15	94.3	98.3	80.3
Sodium sulfite	127	4	29	16	94.5	98.3	80.3
Diphenyl ether	128	1	1.5		94.6	98.3	80.3
Dinitramine	129	2	0.007		94.7	98.3	80.3
Maneb	130	1	1.3		94.8	98.3	80.3
Diethanolamine	131	1	0.2		94.9	98.3	80.3
Tributyl phosphate	132	1	0.3		95	98.3	80.3
Titanium dioxide	133	2	0.5	110	95.1	98.3	80.5
Bromoform	134	1	0.014		95.2	98.3	80.5
Terephthalic acid	135	1	0.18	45	95.3	98.3	80.6
Lignin sulfonate	136	5	180		95.6	98.4	80.6
Propylene	137	1	9.1	660	95.7	98.4	81.6
Uranyl nitrate	138	3	0.21		95.9	98.4	81.6
Nitroaniline	139	1	0.001		96	98.4	81.6
Sodium hydrosulfite	140	2	29	8.4	96.1	98.4	81.6
Toluene-2,4-diamine	141	2	11		96.2	98.4	81.6
Ethylene oxide	142			370	96.2	98.4	82.2
Acetylene	143	1	0.013	5.3	96.3	98.4	82.2
Lead oxide	144	2	2.1	34	96.4	98.4	82.3

TABLE A2: ANALYSIS

CHEMICAL	RANK	SPILL NUMBER	SPILL VOLUME	SUPPLY VOLUME	% NUMBER	% VOLUME	% SUPPLY
Formic acid	145	1	0.2		96.5	98.4	82.3
Endrin	146				96.5	98.4	82.3
Propionic acid	147	1	2		96.6	98.4	82.3
Zinc phosphate	148	1	0.9		96.7	98.4	82.3
Thioglycolic acid	149	1	0		96.8	98.4	82.3
Copper cyanide	150	1	2.2		96.9	98.4	82.3
Isodrin	151				96.9	98.4	82.3
Diallate	152	3	0.06		97.1	98.4	82.3
Ethyl acrylate	153	3	1.1		97.3	98.4	82.3
Asbestos	154	15	310		98.1	98.6	82.3
Mercuric chloride	155				98.1	98.6	82.3
Cesium 137	156	3	0.000003		98.3	98.6	82.3
Cumene	157			45	98.3	98.6	82.4
Carbon dioxide	158	1	0	2500	98.4	98.6	86.1
Chlorine dioxide	159	2	0.3		98.5	98.6	86.1
Fonofos	160			2500	98.5	98.6	89.8
Nitrogen dioxide	161	3	0.001		98.7	98.6	89.8
Endosulfan	162				98.7	98.6	89.8
Aldicarb	163				98.7	98.6	89.8
Calcium carbide	164	1	1.8	82	98.8	98.6	89.9
Potassium carbonate	165	1	100		98.9	98.7	89.9
Tetraethyl pyrophosphate	166				98.9	98.7	89.9
Azinphos ethyl	167				98.9	98.7	89.9
Ethyl mercaptan	168	6	0.01		99.2	98.7	89.9
Calcium arsenate	169	1	0.045		99.3	98.7	89.9
Demeton	170				99.3	98.7	89.9
Nickel carbonyl	171	1	0.3		99.4	98.7	89.9
Sodium nitrate	172	1	2.5		99.5	98.7	89.9
Calcium nitrate	173	1	1.8		99.6	98.7	89.9
Toxaphene	174				99.6	98.7	89.9
Chlorohydrin	175	1	0.8		99.7	98.7	89.9
Aluminum chloride	176			14	99.7	98.7	89.9
Phenyl mercuric acetate	177	1	0.005		99.8	98.7	89.9
Strychnine	178				99.8	98.7	89.9
Cyanogen bromide	179	1	0.00005		99.9	98.7	89.9
Carbon disulfide	180			21	99.9	98.7	89.9
Methoxyethylmercuric acetate	181				99.9	98.7	89.9
Sodium dichromate	182				99.9	98.7	89.9
Cycloheximide	183				99.9	98.7	89.9
DDT	184				99.9	98.7	89.9
Magnesium hydroxide	185	1	11	15	100	98.7	89.9
Hydrocyanic acid	186				100	98.7	89.9
Sodium aluminate	187	1	14	9	100	98.7	89.9
Flamprop-methyl	188	3	0.16		100	98.7	89.9
Triethanolamine	189	1	0.19		100	98.7	89.9
Chloroform	190			3.7	100	98.7	89.9
Disulfoton	191				100	98.7	89.9
Chlorpyrifos	192				100	98.7	89.9
Sodium borohydride	193	1	4.5	17	100	98.7	89.9
Rotenone	194				100	98.7	89.9
Chloroaniline	195	1	0.5		100	98.7	89.9
Cyclohexylamine	196	1	0.07		100	98.7	89.9
Cadmium	197				100	98.7	89.9
Kepone	198				100	98.7	89.9
Acetone cyanohydrin	199				100	98.7	89.9
Acrolein	200				100	98.7	89.9
Arsenic acid	201				100	98.7	89.9
Borax	202			52	100	98.7	90
Ethion	203				100	98.7	90
Mercuric acetate	204				100	98.7	90
Mevinphos	205				100	98.7	90
Cadmium sulfate	206				100	98.7	90
Ethylamine	207	1	1.3		100	98.7	90
Brucine	208				100	98.7	90
Antimony trioxide	209			1500	100	98.7	92.2
Mercuric thiocyanate	210				100	98.7	92.2
Ferric oxide	211	5	23		100	98.7	92.2
Mercurous nitrate	212				100	98.7	92.2
Methiocarb	213				100	98.7	92.2
Acetaldehyde	214			8.5	100	98.7	92.2
Barium sulfate	215	1	820		100	99.3	92.2
Methyl parathion	216				100	99.3	92.2

TABLE A2 ANALYSIS		SPILL	SPILL	SUPPLY	%	%	%
CHEMICAL	RANK	NUMBER	VOLUME	VOLUME	NUMBER	VOLUME	SUPPLY
Phosphorus pentoxide	217	1	0.6		100	99.3	92.2
Dichlone	218				100	99.3	92.2
Hexachlorophene	219				100	99.3	92.2
Sodium chromate	220	1	0.02		100	99.3	92.2
Thiram	221	1	0.3		100	99.3	92.2
Butyl formate	222	1	0.04		100	99.3	92.2
Copper chloride	223				100	99.3	92.2
Sodium azide	224				100	99.3	92.2
Sodium phosphate	225			65	100	99.3	92.3
Allyl alcohol	226				100	99.3	92.3
Urea	227			2600	100	99.3	96.2
Coumaphos	228				100	99.3	96.2
Nitrous oxide	229	1	0.6		100	99.3	96.2
Sodium arsenite	230	1	0		100	99.3	96.2
2,4-Dinitrophenol	213				100	99.3	96.2
Dioxathion	232				100	99.3	96.2
Propargyl alcohol	233				100	99.3	96.2
Ferrous sulfate	234	1	21		100	99.3	96.2
Hexachlorobutadiene	235				100	99.3	96.2
Hydrogen sulfide	236				100	99.3	96.2
Arsine	237	1	0		100	99.3	96.2
2,3,4,6-Tetrachlorophenol	238				100	99.3	96.2
Endothall	239				100	99.3	96.2
Dinitrocresols	240				100	99.3	96.2
Trimethylene bromide	241	1	0.4		100	99.3	96.2
Dicrotophos	242				100	99.3	96.2
Phenolsulfonic acid	243	2	23		100	99.3	96.2
Diphenyl	244	1	1.3		100	99.3	96.2
Glyphosate	245	1	0.003		100	99.3	96.2
Heavy water	246	2	22		100	99.3	96.2
Naled	247				100	99.3	96.2
Hydroquinone	248				100	99.3	96.2
Acrylamide	249				100	99.3	96.2
Vanadium pentoxide	250				100	99.3	96.2
4-Aminopyridine	251				100	99.3	96.2
Ethanolamine	252			15	100	99.3	96.2
EPN	253				100	99.3	96.2
Phosgene	254	1	0		100	99.3	96.2
Phosphine	255	1	0.004		100	99.3	96.2
Lactonitrile	256				100	99.3	96.2
Malononitrile	257				100	99.3	96.2
Mexacarbate	258				100	99.3	96.2
Fluorine	259				100	99.3	96.2
Fluoroacetamide	260				100	99.3	96.2
Arsenic pentoxide	261				100	99.3	96.2
Calcium fluoride	262	1	1		100	99.3	96.2
Ethyleneimine	263				100	99.3	96.2
Sodium hydrosulfide	264	2	2.3		100	99.3	96.2
Aluminum phosphate	265	3	8.5		100	99.3	96.2
Dimethyl ethyl amine	266	1	0		100	99.3	96.2
Tetrahydronaphthalene	267	1	0.09		100	99.3	96.2
Cadmium nitrate	268				100	99.3	96.2
Lead arsenate	269				100	99.3	96.2
Cobaltous chloride	270				100	99.3	96.2
Cadmium chloride	271				100	99.3	96.2
Phosmet	272				100	99.3	96.2
Sulfur chloride	273	3	3.5		100	99.3	96.2
Nicotine sulfate	274				100	99.3	96.2
Boric acid	275			2	100	99.3	96.2
Sodium arsenate	276				100	99.3	96.2
Copper acetate	277				100	99.3	96.2
Nitrophenol	278				100	99.3	96.2
Ferric hydroxide	279	2	5		100	99.3	96.2
Hexachlorocyclopentadiene	280				100	99.3	96.2
Sulfuryl chloride	281	2	4.4		100	99.3	96.2
Crotonaldehyde	282				100	99.3	96.2
Lead fluoroborate	283				100	99.3	96.2
Morpholine	284			0.83	100	99.3	96.2
Stannous chloride	285				100	99.3	96.2
Terphenyl	286	2	1.1		100	99.3	96.2
Benzoyl chloride	287				100	99.3	96.2
Thionyl chloride	288	1	53		100	99.3	96.2

[illegible] ANALYSIS		SPILL	SPILL	SUPPLY	%	%	%
CHEMICAL	RANK	NUMBER	VOLUME	VOLUME	NUMBER	VOLUME	SUPPLY
Trichlorophenoxy propionic acid	289				100	99.3	96.2
Arsenic trioxide	290				100	99.3	96.2
Barban	291	1	0.009		100	99.3	96.2
Zinc acetate	292				100	99.3	96.2
Copper nitrate	293				100	99.3	96.2
Nonane	294	1	0.006		100	99.3	96.2
Trichlorophenol	295				100	99.3	96.2
Yellow cake	296	1	0.21		100	99.3	96.2
Dibromomethane	297				100	99.3	96.2
Dimethyl sulfate	298				100	99.3	96.2
Hexachlorobenzene	299				100	99.3	96.2
Dinitrobenzene	300				100	99.3	96.2
Furfural	301				100	99.3	96.2
Methyl ethyl ketone peroxide	302	1	0		100	99.3	96.2
Stannic chloride	303	1	0		100	99.3	96.2
2,3-Dibromo-1-propanol phosphate	304				100	99.3	96.2
Xylenol	305				100	99.3	96.2
Mercuric sulfide	306	1	30		100	99.3	96.2
Adipic acid	307			72	100	99.3	96.3
Ethyl acetate	308			6.2	100	99.3	96.3
Ethylene dibromide	309				100	99.3	96.3
Nickel chloride	310				100	99.3	96.3
Nitroglycerin	311				100	99.3	96.3
Dodecylbenzenesulfonic acid	312				100	99.3	96.3
Epichlorohydrin	313				100	99.3	96.3
Methyl bromide	314				100	99.3	96.3
Dimethoate	315				100	99.3	96.3
Pyrocatechol	316				100	99.3	96.3
2,4-Dichlorophenol	317				100	99.3	96.3
Trichlorobenzene	318				100	99.3	96.3
Decyl octyl phthalate	319	1	0.1		100	99.3	96.3
Dibutyl amine	320				100	99.3	96.3
Thallium acetate	321				100	99.3	96.3
Sodium fluorosilicate	322				100	99.3	96.3
Thiourea	323				100	99.3	96.3
Benzyl chloride	324				100	99.3	96.3
Temephos	325				100	99.3	96.3
Dinitroaniline	326				100	99.3	96.3
Maleic acid	327				100	99.3	96.3
Quinone	328				100	99.3	96.3
Sodium sulfate	329			410	100	99.3	96.9
Alachlor	330				100	99.3	96.9
Calcium carbonate	331			250	100	99.3	97.3
Sodium nitrilotriacetic acid	332				100	99.3	97.3
Tetramethyl lead	333				100	99.3	97.3
Butylene	334			230	100	99.3	97.6
Glycidyl methacrylate	335				100	99.3	97.6
Pentachlorobenzene	336				100	99.3	97.6
Oleum	337				100	99.3	97.6
Potassium sulfate	338			72	100	99.3	97.7
Butadiene	339				100	99.3	97.7
2,4-Dinitrotoluene	340				100	99.3	97.7
Chlorpropham	341				100	99.3	97.7
Quinoline	342				100	99.3	97.7
Hexachloroethane	343				100	99.3	97.7
Arsenic	344				100	99.3	97.7
Butyl mercaptan	345				100	99.3	97.7
Propylene chlorohydrin	346	1	5.9		100	99.3	97.7
Dichlorodifluoromethane	347				100	99.3	97.7
N-Nitrosodiphenylamine	348				100	99.3	97.7
Potassium dichromate	349				100	99.3	97.7
Benzophenone	350				100	99.3	97.7
Dichloroethyl ether	351				100	99.3	97.7
Chlorobenzene	352				100	99.3	97.7
2-Phenylphenol	353				100	99.3	97.7
Allyl chloride	354				100	99.3	97.7
Benzaldehyde	355				100	99.3	97.7
Diuron	356				100	99.3	97.7
Phenylenediamine	357	1	0		100	99.3	97.7
1,2,4,5-Tetrachlorobenzene	358				100	99.3	97.7
Adiponitrile	359				100	99.3	97.7
Decyl alcohol	360				100	99.3	97.7

TABLE A1. ANALYSIS		SPILL	SPILL	SUPPLY	%	%	%
CHEMICAL	RANK	NUMBER	VOLUME	VOLUME	NUMBER	VOLUME	SUPPLY
Furfuryl alcohol	361				100	99.3	97.7
Nitrosodimethylamine	362				100	99.3	97.7
Nonanol	363				100	99.3	97.7
Cobaltous hydroxide	364	1	5.1		100	99.3	97.7
Magnesium oxide	365	1	5		100	99.3	97.7
Resorcinol	366				100	99.3	97.7
Tetrachloroethylene	367				100	99.3	97.7
Sodium phosphate, tribasic	368				100	99.3	97.7
Acetophenone	369				100	99.3	97.7
Benzonitrile	370				100	99.3	97.7
Chromous chloride	371				100	99.3	97.7
Cobaltous bromide	372				100	99.3	97.7
Diisopropylamine	373				100	99.3	97.7
Hexanol	374				100	99.3	97.7
Nitrobenzene	375				100	99.3	97.7
Nitrotoluene	376				100	99.3	97.7
Oleic acid	377			2.6	100	99.3	97.7
Tridecyl alcohol	378				100	99.3	97.7
Trimethylamine	379	1	1.5		100	99.3	97.7
Chlorodifluoromethane	380	1	0.22		100	99.3	97.7
Methyl hexyl ketone	381	1	0.94		100	99.3	97.7
Isobutyl acrylate	382				100	99.3	97.7
Potassium aluminate	383	1	0.7		100	99.3	97.7
Chloroethylvinyl ether	384				100	99.3	97.7
Triethylamine	385				100	99.3	97.7
Eptam	386				100	99.3	97.7
Sodium	387	1	0.5		100	99.3	97.7
Anthracene	388				100	99.3	97.7
Butylamine	389				100	99.3	97.7
Dimefox	390				100	99.3	97.7
Iodomethane	391				100	99.3	97.7
Phorate	392				100	99.3	97.7
Sodium fluoroacetate	393				100	99.3	97.7
Sulfotepp	394				100	99.3	97.7
Zinc bromide	395	1	0.38		100	99.3	97.7
Atlox	396	1	0.2		100	99.3	97.7
Benzidine	397				100	99.3	97.7
Sodium thioglycolate	398	1	0.2		100	99.3	97.7
Lithium bromide	399	1	0.13		100	99.3	97.7
Ammonium stearate	400	1	0.1		100	99.3	97.7
Crimidine	401				100	99.3	97.7
Isovaleraldehyde	402				100	99.3	97.7
Caprolactam	403			12	100	99.3	97.7
Benzyl alcohol	404				100	99.3	97.7
Methylstyrene	405				100	99.3	97.7
Sodium bisulfite	406				100	99.3	97.7
Dichlobenil	407				100	99.3	97.7
Diphacinone	408				100	99.3	97.7
Diphenylamine	409	1	0.03		100	99.3	97.7
Fumaric acid	410			1.2	100	99.3	97.7
Oxalic acid	411			1.1	100	99.3	97.7
Nitralin	412				100	99.3	97.7
Toluidine	413				100	99.3	97.7
Warfarin	414				100	99.3	97.7
Neopentyl glycol	415	1	0.01		100	99.3	97.7
Benzyl-n-butyl phthalate	416				100	99.3	97.7
Diethyl-p-nitrophenyl phosphate	417				100	99.3	97.7
Furazolidone	418				100	99.3	97.7
Carbonyl sulfide	419				100	99.3	97.7
Dalapon	420				100	99.3	97.7
N,N-Dimethylaniline	421				100	99.3	97.7
Valeraldehyde	422				100	99.3	97.7
Chlorophacinone	423				100	99.3	97.7
Fensulfothion	424				100	99.3	97.7
Methanesulfonyl fluoride	425				100	99.3	97.7
Metobromuron	426				100	99.3	97.7
Nitrilotriacetic acid	427				100	99.3	97.7
Chloroxuron	428				100	99.3	97.7
Dichloroethylene	429				100	99.3	97.7
Diethyl-m-toluamide	430				100	99.3	97.7
Methyl phenkapton	431				100	99.3	97.7
Dimethylaniline	432	1	0.005		100	99.3	97.7

[illegible] ANALYSIS		SPILL	SPILL	SUPPLY	%	%	%
CHEMICAL	RANK	NUMBER	VOLUME	VOLUME	NUMBER	VOLUME	SUPPLY
Ammonium picrate	433				100	99.3	97.7
Diphenylmethane-4,4'-diisocyanate	434				100	99.3	97.7
Propionaldehyde	435				100	99.3	97.7
Strychnine sulfate	436				100	99.3	97.7
Isooctyl alcohol	437				100	99.3	97.7
Methyl isobutyl ketone	438			8.7	100	99.3	97.7
Phenanthrene	439				100	99.3	97.7
Hexaldehyde	440				100	99.3	97.7
Hydrogen	441			1200	100	99.3	99.5
Phenylthiourea	442				100	99.3	99.5
Amiton	443				100	99.3	99.5
Beryllium	444				100	99.3	99.5
Bromine	445				100	99.3	99.5
Heptanol	446				100	99.3	99.5
Nitropropane	447				100	99.3	99.5
Octanol	448				100	99.3	99.5
Sodium anthraquinone sulfate	449				100	99.3	99.5
Glycerine	450			7.7	100	99.3	99.5
Silver nitrate	451				100	99.3	99.5
Butyric acid	452				100	99.3	99.5
Fluoranthene	453				100	99.3	99.5
Naphthol	454				100	99.3	99.5
Fluoroacetic acid	455				100	99.3	99.5
Propionic anhydride	456				100	99.3	99.5
Sulfamic acid	457				100	99.3	99.5
Ammonium sulfamate	458				100	99.3	99.5
Carboxymethylcellulose	459			2.5	100	99.3	99.5
Cyclohexanone	460				100	99.3	99.5
Dibutyl ether	461				100	99.3	99.5
Dithiobiuret	462				100	99.3	99.5
Isobenzan	463				100	99.3	99.5
Ethylene glycol monobutyl ether	464				100	99.3	99.5
Butyraldehyde	465			0.2	100	99.3	99.5
Chromic sulfate	466				100	99.3	90.5
Dimethyl phthalate	467				100	99.3	99.5
Melamine	468			6.8	100	99.3	99.5
Fluenetil	469				100	99.3	99.5
Nitromethane	470				100	99.3	99.5
Choline chloride	471			5.8	100	99.3	99.5
Isophorone	472				100	99.3	99.5
Naphtha	473				100	99.3	99.5
Turpentine	474			11	100	99.3	99.5
1,1-Dichloropropane	475				100	99.3	99.5
2,2'-Thiobis(4,6-dichlorophenol)	476				100	99.3	99.5
Hexaethyl tetraphosphate	477				100	99.3	99.5
Sodium selenite	478				100	99.3	99.5
5-[Bis(2-chloroethyl)amino] uracil	479				100	99.3	99.5
Camphor oil	480				100	99.3	99.5
Dichloroethyl amino uracil	481				100	99.3	99.5
Methyl amyl alcohol	482				100	99.3	99.5
Monocrotophos	483				100	99.3	99.5
Mephosfolan	484				100	99.3	99.5
Thallium	485				100	99.3	99.5
Chromium	486				100	99.3	99.5
Ethylene thiourea	487				100	99.3	99.5
Lead chloride	488				100	99.3	99.5
Thiosemicarbazide	489				100	99.3	99.5
Acetyl chloride	490				100	99.3	99.5
Cantharidin	491				100	99.3	99.5
Isobutyl alcohol	492			1.5	100	99.3	99.5
Propylamine	493				100	99.3	99.5
Diethyl chlorophosphate	494				100	99.3	99.5
Isopropylmethylpyrazolyl dimethylca	495				100	99.3	99.5
Potassium chlorate	496				100	99.3	99.5
Bisphenol A	497			1.9	100	99.3	99.5
Diethyl phthalate	498				100	99.3	99.5
Salicylic acid	499				100	99.3	99.5
Fluometuron	500				100	99.3	99.5
Iodine	501				100	99.3	99.5
Potassium arsenite	502				100	99.3	99.5
Acetonitrile	503				100	99.3	99.5
Dioctyl phthalate	504			18	100	99.3	99.5

TABLE A1: ANALYSIS CHEMICAL	RANK	SPILL NUMBER	SPILL VOLUME	SUPPLY VOLUME	% NUMBER	% VOLUME	% SUPPLY
Ethylene glycol diacetate	505				100	99.3	99.5
Acridine	506				100	99.3	99.5
Amyl alcohol	507				100	99.3	99.5
Formaldehyde cyanohydrin	508				100	99.3	99.5
Tetraethyltin	509				100	99.3	99.5
Coumatetralyl	510				100	99.3	99.5
Cyclohexanol	511				100	99.3	99.5
Ethylenediaminetetraacetic acid	512				100	99.3	99.5
Mercuric oxide	513				100	99.3	99.5
Propyleneimine	514				100	99.3	99.5
TOTALS		1947	138139.7	67145.9			

TABLE A4

LISTS OF PRIORITY SUBSTANCES

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O – SARA LIST OF EXTREMELY HAZARDOUS
P – CERCLA HAZARDOUS SUBSTANCES
R – RCRA HAZARDOUS LIST
S – CEPA PRIORITY SUBSTANCES
Q – SARA SECTION 313
X – TOP 100 MEMBERSHIP, Y – TOP 250, Z – TOP 500

SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Acenaphthene				X	X		X									X			
Acenaphthylene				X			X									X			
Acetaldehyde	Y		X			X	X	X		X	X	X		X		X	X	X	
Acetamide																	X		
Acetic acid	X	X	X			X	X	X		X		X	X	X		X			
Acetic anhydride	X	X	X			X	X	X		X		X	X	X		X			
Acetoacetanilide																			
Acetone	X	X	X			X		X		X		X	X	X		X	X	X	
Acetone cyanohydrin	Y		X				X		X	X	X	X			X	X		X	
Acetone thiosemicarbazide									X										
Acetonitrile			X			X		X		X						X	X	X	
Acetophenone	Z		X													X		X	
Acetyl bromide			X				X			X						X			
Acetyl chloride	Z		X				X	X		X	X					X		X	
Acetyl peroxide			X							X									
Acetylacetone			X																
Acetylene	X	X	X							X	X		X						
Acrolein	Y		X	X	X		X	X	X	X	X				X	X	X	X	
Acrylamide	Y		X						X	X					X	X	X	X	
Acrylic acid			X			X		X		X		X				X	X		
Acryloyl chloride									X						X				
Acrylonitrile	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Adipic acid	Z	X	X				X			X		X				X			
Adiponitrile	Z		X					X	X	X		X			X				
Alachlor	Z																		
Aldicarb	Y																		
Aldrin	X		X	X	X		X		X	X			X		X	X	X	X	
Alkyl benzenesulfonic acid			X																
Allyl alcohol			X				X	X	X	X					X	X		X	
Allylamine									X						X				
Allyl bromide			X							X									
Allyl chloride	Z		X				X			X						X	X		
Allyl chloroformate			X							X									
Allyltrichlorosilane			X							X									
Aluminum																	X		
Aluminum chloride	Y	X	X							X									
Aluminum fluoride			X																
Aluminum hydroxide		X																	
Aluminum nitrate			X							X									
Aluminum oxide																	X		
Aluminum phosphate	Z									X			X				X		
Aluminum sulfate	X	X	X				X	X		X		X	X			X			
2-Aminoanthraquinone																	X		
Aminocarb	X	X																	
Aminoethylethanolamine			X																
1-Amino-2-methyl anthraquinone																			
4'-Amino propiophenone																			
Aminopterin									X						X				
Amiton	Z								X						X				
Amitrole																X	X	X	
Ammonia	X	X	X			X	X	X	X	X	X	X	X	X	X	X	X		
Ammonium acetate			X				X			X						X			
Ammonium benzoate			X				X			X						X			
Ammonium bicarbonate			X				X			X						X			
Ammonium bisulfate										X									
Ammonium bisulfite							X			X						X			
Ammonium carbamate							X			X						X			
Ammonium carbonate			X				X			X						X			
Ammonium chlorate										X									
Ammonium chloride	X	X	X				X			X			X			X			

TABLE A4 — LISTS OF PRIORITY SUBSTANCES

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S = CEPA PRIORITY SUBSTANCES
Q = SARA SECTION 313
X = TOP 100 MEMBERSHIP, Y = TOP 250, Z = TOP 500

SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Ammonium chromate							X			X						X			
Ammonium citrate			X				X			X						X			
Ammonium dichromate			X				X			X						X			
Ammonium fluoride			X				X			X						X			
Ammonium fluoroborate							X			X						X			
Ammonium formate			X																
Ammonium hydrogen fluoride			X				X			X						X			
Ammonium hydroxide	X		X				X	X		X			X			X			
Ammonium iodide			X																
Ammonium molybdate			X																
Ammonium nitrate	X	X	X							X	X	X	X	X			X		
Ammonium nitrate-phosphate mix.			X							X	X								
Ammonium nitrate-sulfate mixture			X							X	X								
Ammonium oleate			X																
Ammonium oxalate			X			X				X						X			
Ammonium pentaborate			X																
Ammonium pentachloride																			
Ammonium perchlorate			X							X									
Ammonium persulfate			X							X									
Ammonium phosphate dibasic	X	X	X										X						
Ammonium phosphate hemibasic	X	X	X										X						
Ammonium phosphate monobasic	X	X	X										X						
Ammonium picrate	Z									X	X					X		X	
Ammonium silicofluoride			X			X				X						X			
Ammonium stearate	Z		X										X						
Ammonium sulfamate	Z		X			X	X			X						X			
Ammonium sulfate	X	X	X									X	X				X		
Ammonium sulfide			X			X	X			X									
Ammonium sulfite			X				X			X									
Ammonium tartrate			X				X			X						X			
Ammonium thiocyanate			X				X			X						X			
Ammonium thiosulfate			X				X	X		X									
Ammonium vanadate																X			
Amyl acetate			X				X			X						X			
Amyl alcohol			X					X		X									
Amyl chloride			X							X									
Amyl mercaptan			X							X									
Amyl methy ketone			X							X									
Amyl nitrate			X							X									
Amyltrichlorosilane			X							X									
Aniline	X		X			X	X	X	X	X		X	X	X	X	X	X	X	X
Anisidine										X							X		
Anisoyl chloride			X							X									
Anthracene	Z		X	X			X									X	X		
Antimony				X	X		X			X						X	X		
Antimony pentachloride			X		X		X			X						X			
Antimony pentafluoride			X		X				X	X	X				X				
Antimony potassium tartrate			X		X		X			X						X			
Antimony tribromide					X		X			X						X			
Antimony trichloride					X		X			X						X			
Antimony trifluoride					X		X			X						X			
Antimony trioxide	Y		X		X		X			X						X			
Antimycin A									X						X			X	
Arsenic	Z			X	X					X						X	X	X	X
Arsenic acid	Y		X		X	X				X						X		X	
Arsenic disulfide			X		X		X			X						X			
Arsenic pentoxide	Z				X		X		X						X	X		X	
Arsenic trichloride			X		X		X			X					X	X			
Arsenic trioxide	Z		X		X	X	X	X		X									
Arsenic trisulfide			X		X		X			X						X			

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Arsine	Y	X							X	X	X		X		X				
Asbestos	Y			X	X					X			X			X	X		X
Asphalt			X							X									
Atlox	Z												X						
Atrazine	X		X										X						
Azinphosethyl	Y								X						X				
Azinphosmethyl	X		X						X	X	X		X		X	X			
Barban	Z												X						
Barium										X							X	X	
Barium carbonate			X																
Barium chlorate			X							X									
Barium chloride																			
Barium cyanide							X			X						X		X	
Barium nitrate			X							X									
Barium perchlorate			X							X									
Barium permanganate			X							X									
Barium peroxide			X							X									
Barium sulfate	Y		X										X						
Benazolin																			
Bentonite																			
Benzaldehyde	Z		X							X									
Benzamine																			
Benzene	X	X	X	X	X	X	X	X		X		X	X	X		X	X	X	X
Benzenearsonic acid									X							X			
Benzene hexachloride (BHC)	X		X	X	X		X		X				X		X	X	X	X	
Benzene phosphorus dichloride			X							X									
Benzene phosphorus thiodichloride			X							X									
Benzenesulfonyl chloride									X						X	X		X	
Benzidine	Z			X	X					X						X	X	X	X
1,2-Benzisothiazolin-3-one 1,1-dioxide																			
Benzo[b]fluoranthene				X															
Benzo[ghi] perylene							X									X			
Benzo[k]fluoranthene																			
Benzoic acid	X	X	X				X			X			X			X			
Benzonitrile	Z		X				X			X						X			
Benzophenone	Z		X																
Benzoquinone							X			X						X	X	X	
Benzotrichloride									X						X	X	X	X	
Benzotrifluoride	X									X			X						
Benzoyl chloride	Z		X			X	X			X						X	X		
Benzoyl peroxide			X							X	X						X		
Benzyl alcohol			X																
Benzyl bromide			X							X									
Benzyl-n-butyl phthalate	Z		X	X												X	X		
Benzyl chloride	Z		X			X	X	X	X	X					X	X	X	X	
Benzyl chloroformate			X							X									
Benzyl cyanide									X						X				
Benzylamine			X																
Benzyldimethyloctadecylammonium chloride			X																
Benzyltrimethylammonium chloride			X																
Benz[a]anthracene				X												X		X	
Benz[a]acridine																			
Beryllium	Z		X	X	X					X	X					X	X	X	
Beryllium chloride			X		X		X			X						X			
Beryllu fluoride			X		X		X			X						X			
Beryllium nitrate			X		X		X			X						X			
Beryllium oxide			X		X														
Beryllium sulfate			X		X														
Bismuth oxychloride			X																
Bisphenol A	Z		X									X							

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Bisphenol A diglycidyl ether			X																
Boric acid	Z	X	X																
Boron tribromide			X							X									
Boron trichloride			X						X	X	X				X				
Boron trifluoride									X	X	X				X				
Bromine	Z		X						X	X	X				X				
Bromine pentafluoride			X							X	X								
Bromine trifluoride			X							X	X								
Bromoacetone										X						X		X	
Bromobenzene			X							X									
Bromochlorodifluoromethane																			
Bromoform	X			X						X			X			X	X	X	
1-Bromo-4-phenoxy benzene																			
Bromotrifluoromethane										X									
Bromoxynil																			
Brucine	Y		X							X						X		X	
BTX																			
1,3-Butadiene	Z	X	X						X	X	X	X		X	X		X		
Butane			X							X	X								
1,4-Butanediol			X									X							
1,4-Butenediol			X																
Butyl acetate			X			X	X	X		X						X			
Butyl acrylate			X					X		X		X					X		
Butyl alcohol	X	X	X					X		X		X	X	X		X	X	X	
Butyl formate	Y									X			X						
Butyl hydroperoxide			X							X									
Butyl isovalerate									X						X				
Butyl mercaptan	Z		X							X									
Butyl methacrylate			X							X									
Butyl peroxy-2-ethylhexanoate										X	X								
Butyl peroxypivalate										X	X								
Butyl phenol			X							X									
Butylamine	Z		X				X	X		X						X			
Butylated hydroxytoluene																			
Butylene	Z	X	X							X	X								
Butylene oxide			X							X							X		
Butyltrichlorosilane			X							X									
Butyraldehyde	Z	X	X					X		X		X		X			X		
Butyric acid	Z		X				X	X		X						X			
Cacodylic acid			X							X						X		X	
Cadmium	Y			X	X											X	X	X	X
Cadmium acetate			X		X		X			X						X			
Cadmium bromide			X		X		X			X						X			
Cadmium chloride	Z		X		X		X		X										
Cadmium fluoroborate			X		X														
Cadmium nitrate	Z		X		X														
Cadmium oxide			X		X				X						X				
Cadmium sulfate	Y		X		X														
Cadmium stearate					X				X						X				
Calcium arsenate	Y		X				X		X	X			X		X	X			
Calcium carbide	Y	X	X			X	X			X	X		X	X		X			
Calcium carbonate	Z	X																	
Calcium chlorate			X							X									
Calcium chloride	X	X	X									X	X						
Calcium chromate			X				X			X									
Calcium cyanamide										X									
Calcium cyanide	X		X				X			X	X		X			X		X	
Calcium dodecylbenzenesulfonate			X				X			X									
Calcium fluoride	Z		X										X						
Calcium formate																			

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Calcium hydroxide	X	X	X					X					X						
Calcium hypochlorite	X	X	X				X			X			X			X			
Calcium nitrate	Y		X							X			X						
Calcium oxide	X	X	X							X		X	X						
Calcium peroxide			X							X									
Calcium phosphate	X	X	X										X						
Calcium phosphide			X							X	X								
Calcium propionate hydrate																			
Calcium resinate			X							X									
Calcium sulfate dihydrate																			
Camphene			X							X									
Camphor oil	Z		X							X									
Cantharidin	Z								X						X				
Caprolactam	Z	X	X									X							
Caprylic acid																			
Captan			X				X			X						X	X		
Carbachol chloride									X						X				
Carbamidoselenic acid							X									X		X	
Carbaryl	X	X	X				X			X			X			X	X		
Carbofuran	X	X					X		X	X			X		X	X			
Carbolic oil			X																
Carbon dioxide	Y	X	X							X		X	X	X					
Carbon disulfide	Y	X	X			X	X		X	X	X			X	X	X	X	X	
Carbon monoxide			X							X	X								
Carbon tetrachloride	X	X	X	X	X		X	X		X		X	X			X	X	X	
Carbophenothion									X										
Carboxymethylcellulose	Z																		
Carene			X																
Catechol			X														X		
Cesium 137	Y												X						
Cetyl alcohol																			
Charcoal			X							X									
Chloramben																	X		
Chlordane	X	X	X	X	X		X	X	X	X	X		X		X	X	X	X	
Chlorine	X	X	X			X	X	X	X	X	X	X	X	X					
Chlorine dioxide	Y									X			X						
Chlorine trifluoride			X							X	X								
Chlormequat																			
Chloroacetophenone			X							X							X		
Chloroacetic acid			X					X	X	X									
Chloroacetyl chloride			X							X					X	X		X	
Chloroaniline	Y		X							X			X						
Chlorobenzene	Z		X	X	X		X	X		X						X	X	X	X
Chloro benzoyl peroxide										X									
4-Chlorobutyronitrile			X																
p-Chloro-m-cresol				X						X						X		X	
4-Chloro-2-cyclopentyl phenol																			
Chlorodibromomethane				X												X			
5-Chloro-2-(2,4-dichlorophenoxy)phenol																			
Chlorodifluoroethane										X	X								
Chlorodifluoromethane	Z		X							X			X						
2-Chloro-4,6-dinitrophenol																			
2-Chloroethyl vinyl ether	Z			X												X		X	
Chloroform	Y	X	X	X	X		X	X	X	X					X	X	X	X	
Chlorohydrin	Y		X																
Chloromercuri dinitriophenol																			
Chloromercuriphenol																			
Chloromethyl methyl ether			X	X					X	X					X	X	X	X	X
1-(Chloromethyl)-4-nitrobenzene									X						X				
Chloronaphthalene				X	X											X		X	

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Chloronitrobenzene										X									
Chloro nitrophenol																			
Chloro nitrophenol, sodium salt																			
Chloropentafluoroethane										X									
Chlorophacinone	Z								X				X		X				
m-Chlorophenol	X				X					X									
o-Chlorophenol	X		X	X	X					X						X		X	
p-Chlorophenol	X		X		X					X									
Chlorophenol, potassium salt																			
(2-Chlorophenyl) thiourea															X	X		X	
Chloro phenyl phenol																			
Chloropicrin			X							X	X								
Chloroprene										X							X		
3-Chloropropionitrile									X						X	X		X	
Chlorosulfonic acid			X				X			X	X					X			
Chlorothalonil																	X		
Chlorotoluidine			X							X									
Chlorotoluidine hydrochloride										X									
Chlorotrifluoromethane										X									
Chloroxuron	Z								X										
Chlorpropham	Z																		
Chlorpyrifos	Y						X			X						X			
Choline chloride	Z																		
Chromic acetate							X			X						X			X
Chromic acid	X		X				X			X			X			X			X
Chromic sulfate	Z						X			X			X						X
Chromium	Z			X	X											X	X	X	X
Chromous chloride	Z				X		X			X			X						X
Chromyl chloride			X		X														X
Citric acid			X																
Coal tar																			
Cobalt									X						X		X		
Cobaltous acetate			X																
Cobaltous bromide	Z						X			X						X			
Cobaltous chloride	Z		X																
Cobaltous formate							X			X						X			
Cobaltous hydroxide	Z												X						
Cobaltous nitrate	X		X										X						
Cobaltous sulfamate							X			X									
Cobaltous sulfate			X																
Copper				X	X		X									X	X		
Copper acetate	Z		X		X		X			X						X			
Copper acetoarsenite			X		X		X			X									
Copper arsenite			X		X					X									
Copper bromide			X		X														
Copper chloride	Y		X		X		X			X						X			
Copper cyanide	X		X		X					X	X		X			X		X	
Copper fluoroborate			X		X														
Copper hydroxide					X														
Copper iodide			X		X														
Copper naphthenate			X		X														
Copper nitrate	Z		X		X		X			X						X			
Copper oxalate			X		X		X			X						X			
Copper oxide					X								X						
Copper sulfate	X	X	X		X		X	X		X			X			X			
Copper sulfate, ammoniated					X		X			X									
Copper tartrate							X			X						X			
Coumafuryl									X						X				
Coumaphos	Y		X				X		X	X	X				X	X			
Coumatetralyl									X						X				

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
p-Cresidine																	X		
Creosote, coal tar			X			X				X									X
Cresols		X	X				X	X		X			X		X	X	X	X	
Crimidine	Z								X						X				
Crotonaldehyde	Z		X				X		X	X					X	X		X	
Cumene	Y		X						X	X		X							
Cumene hydroperoxide			X							X									
Cupferron																	X		
Cupriethylenediamine			X							X									
Cyanoacetic acid			X																
Cyanogen			X							X	X					X		X	
Cyanogen bromide	Y		X						X	X			X		X	X		X	
Cyanogen chloride			X				X			X	X					X		X	
Cyanogen iodide									X						X				
Cyanophos									X						X				
Cyanuric acid																			
Cyanuric fluoride									X						X				
Cyclohexane	X	X	X			X	X	X		X		X	X	X		X	X	X	
Cyclohexanol			X									X							
Cyclohexanone	Z		X							X						X	X	X	
Cyclohexanone peroxide			X							X	X								
Cyclohexenyltrichlorosilane			X							X									
Cycloheximide	Y								X						X				
Cyclohexylamine	Y		X						X	X			X		X				
Cyclopentane			X						X	X					X				
Cyclophosphamide																X		X	
Cyclopropane			X							X	X								
Cymene			X							X									
2,4-D		X	X				X	X		X			X			X	X	X	
2,4-D esters			X				X			X						X			
Dalapon	Z		X					X								X			
DDD			X	X			X									X		X	
DDE				X											X				
DDT	Y		X	X	X		X			X						X		X	
Decaborane			X						X	X									
Decabromodiphenyl oxide																	X		
Decahydronaphthalene			X							X									
Decaldehyde			X																
Decane			X																
Decyl alcohol	Z		X							X									
Decyl benzene			X										X						
Decyl octyl phthalate	Z																		
Demeton	Y								X										
Demeton-S-methyl									X						X				
Diacetone alcohol			X							X									
Diallate	Y												X			X	X	X	
4,4'-Diaminodiphenyl ether										X								X	
Diamyl phthalate			X																
Diazinon	X		X				X			X			X			X			
Diazomethane																	X		
Dibenzofuran																	X		
Dibenzo(a,h)anthracene				X												X		X	
1,2:7,8-Dibenzopyrene																X		X	
1,2-Dibromo-3-chloropropane																X	X	X	
Dibromomethane	Z									X						X	X	X	
2,3-Dibromo-1-propanol phosphate																X	X	X	
Dibutyl amine	Z		X							X									
Dibutyl ether	Z		X					X		X									
Dibutyl ketone			X																
Dibutyl phthalate			X	X					X						X	X	X	X	X

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Dibutyl phenol			X																
Dicamba	X	X					X			X			X			X			
Dichlobenil	Z						X			X						X			
Dichlone	Y						X			X						X			
Dichlorobenzene		X	X	X	X		X			X						X	X	X	X
Dichlorobenzidine				X	X														X
Di(p-chlorobenzoyl)peroxide			X								X								
3,3'-Dichloro(1,1'-biphenyl)-4,4'-diamine																X	X	X	
Dichlorobromomethane				X												X	X		
Dichlorobutene			X							X					X				
Dichlorodifluoroethane																			
Dichlorodifluoromethane	Z		X	X						X						X		X	
1,1-Dichloroethane				X						X						X		X	
Dichloroethoxy methane																			
Dichloroethyl amino uracil	Z																		
3-(p-Di(chloroethyl)amino) phenyl-L-alanine																X		X	
Dichloro ethyl ether	Z		X						X						X	X	X	X	
1,1-Dichloroethylene	Z		X	X		X	X	X		X				X		X	X	X	
1,2-Dichloroethylene	Z		X	X		X				X						X		X	
Dichlorofluoromethane										X									
Dichloroisopropyl ether										X									
Dichloro methyl ether															X	X	X	X	X
Dichloromethyl ketone																			
2,4-Dichlorophenol			X	X	X											X	X	X	
3,4-Dichlorophenyl isocyanate									X	X	X								
1,1-Dicloropropane			X				X			X						X			
1,2-Dichloropropane			X	X	X		X	X		X						X	X	X	
1,3-Dichloropropane								X		X						X			
1,2-Dichloropropene			X	X	X		X			X									
1,3-Dichloropropene			X				X			X						X	X	X	
Dichlorotetrafluoroethane										X									
4,4-Dichlorotrichloromethylbenhydrol			X																
Dichlorvos	X						X		X	X			X		X	X	X		
Dicrotophos	Y								X						X				
Dicumyl peroxide										X									
Dicyclopentadiene			X							X									
Dieldrin	X		X	X			X			X			X			X		X	
Diepoxybutane									X						X	X	X	X	
Diethanolamine	Y		X					X					X				X		
Diethanolamine lauryl sulfate			X																
Diethyl carbonate			X							X									
Diethyl chlorophosphate	Z														X				
Diethyl methyl amine													X						
Diethyl phthalate			X	X												X	X	X	
Diethyl sulfate										X					X				
Diethyl-m-toluamide	Z																		
Diethyl-p-nitrophenyl phosphate	Z															X		X	
Diethylamine	X		X				X	X					X			X			
Diethylbenzene			X																
Diethylene glycol			X									X							
Diethylene glycol dimethyl ether			X																
Diethylene glycol monobutyl ether			X																
Diethylene glycol monobutyl ether acetate			X																
Diethylene glycol monoethyl ether			X																
Diethylene glycol monoethyl ether acetate																			
Diethylene glycol monomethyl ether			X																
Diethylenetriamine			X							X									
Diethylhexyl phosphoric acid			X																
Diethylzinc			X																
Difluoroethane			X							X									

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Difluorophosphoric acid			X							X									
Diheptyl phthalate			X													X		X	
1,2-Dihydro-3-methyl benz[j]aceanthrylene																			
Diisobutyl ketone			X							X									
Diisobutylcarbinol			X																
Diisobutylene			X							X									
Diisodecyl phthalate			X																
Diisopropanolamine			X																
Diisopropylamine	Z		X							X									
Diisopropylbenzene hydroperoxide			X							X									
Dimefox	Z								X						X				
Dimethoate	Z								X						X	X		X	
Dimethyl (4-methylthio) phenyl phosphate																			
Dimethylacetamide			X																
3,3'-Dimethyl(1,1'-biphenyl)-4,4'-diamine																X	X	X	
Dimethyl carbamoyl chloride										X						X	X	X	
Dimethyl ether		X	X							X	X								
Dimethyl ethyl amine	Z												X						
Dimethyl formamide			X							X									
Dimethyl hydrazine			X						X	X	X				X	X	X	X	
Dimethyl phosphorochloidothioate									X										
Dimethyl phthalate	Z			X					X						X	X	X	X	
Dimethyl sulfate	Z		X						X	X					X	X	X	X	
Dimethyl sulfide			X						X	X					X				
Dimethyl sulfoxide			X																
Dimethyl terephthalate		X	X																
Dimethyl-p-phenylenediamine									X										
Dimethylamine	X		X				X	X		X	X		X			X		X	
Dimethylaniline	Z												X						
Dimethyldichlorosilane			X						X	X	X					X			
Dimethylhexane dihydroperoxide			X							X	X								
Dimethylphenethylamine																X			
Dimethylpolysiloxane			X																
Dimethylzinc			X							X	X								
Dimetilan									X										
Dinitramine	X												X						
Dinitroaniline	Z		X							X									
Dinitrobenzene	Z		X				X			X	X					X			
Dinitrocresols	Y		X	X					X	X					X	X	X	X	
2,4-Dinitrophenol			X	X			X			X	X					X	X	X	
2,6-Dinitrophenol							X			X	X					X			
2,4-Dinitrotoluene			X	X	X		X			X						X	X	X	
2,6-Dinitrotoluene				X	X		X			X						X	X	X	
3,4-Dinitrotoluene					X		X			X						X			
Dinoseb	X	X							X				X		X	X		X	
Dinoterb									X						X				
Dioctyl adipate			X														X		
Dioctyl phthalate			X	X					X						X	X	X	X	X
Dioctyl sodium sulfosuccinate			X																
Dioxane			X							X						X	X	X	
Dioxathion	Y														X				
Dioxolane									X	X					X				
Dipentene			X							X									
Diphacinone	Z								X						X				
Diphenyl	Y												X						
Diphenyl ether	X		X										X						
Diphenylamine	Z		X										X						
Diphenyldichlorosilane			X							X									
Diphenylguanidine																			
1,2-Diphenylhydrazine				X	X											X	X	X	

TABLE A4

LISTS OF PRIORITY SUBSTANCES

A = 1980 PRIORITY LIST
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C = U.S. COAST GUARD CHRIS LIST
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O = SARA LIST OF EXTREMELY HAZARDOUS
P = CERCLA HAZAPDOUS SUBSTANCES
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S = CEPA PRIORITY SUBSTANCES
Q = SARA SECTION 313
X = TOP 100 MEMBERSHIP, Y = TOP 250, Z = TOP 500

SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Diphenylmethane-4,4'-diisocyanate	Z	X	X							X							X		
Dipropylamine			X							X						X		X	
Dipropylene glycol			X																
Dipropylnitrosamine																X	X	X	
Diquat	X						X			X			X			X			
Disodium arsenite																			
Disodium hexafluorosilicate																			
Disodium nitrilotriacetate acid	Z		X																
Disulfoton	Y						X		X	X	X				X	X		X	
Dithiazanine iodide									X						X				
Dithiobiuret									X						X	X		X	
Dithiocarbamate										X	X								
Diuron							X			X						X			
Dodecene			X									X							
Dodecyl mercaptan																			
Dodecylbenzene			X					X											
Dodecylbenzenesulfonic acid	Z						X			X									
Dodecyltrichlorosilane			X							X									
Dowtherm			X																
Endosulfan	Y			X	X		X		X	X					X	X		X	
Endothall	Y															X		X	
Endothion									X						X				
Endrin	X		X	X	X		X		X	X					X	X		X	
Epichlorohydrin	Z		X				X	X	X	X		X			X	X	X	X	
EPN	Z								X						X				
Eptam	Z																		
Ethane			X							X	X								
1,2-Ethanediylbis carbamodithioc acid																X		X	
Ethanethioamide																X	X	X	
Ethanolamine	Z	X	X							X		X							
Ethion	Y						X	X	X	X	X				X	X			
Ethoxy triglycol			X																
Ethoxydihydropyran			X																
Ethoxyquin																			
Ethyl 4,4'-dichlorobenzilate																X	X	X	
Ethyl acetate	Z		X			X		X		X						X		X	
Ethyl acetoacetate			X																
Ethyl acrylate	Y		X			X		X		X			X	X		X	X	X	
Ethyl alcohol	X	X	X					X		X		X	X						
Ethyl butanol			X							X									
Ethyl butyrate			X							X									
Ethyl chloride	X		X							X	X		X	X		X	X		
Ethyl chloroacetate			X							X									
Ethyl chloroformate			X							X							X		
Ethyl ether			X							X									
Ethyl formate			X							X									
Ethyl hexyl tallate			X																
Ethyl lactate			X							X									
Ethyl mercaptan	Y		X							X			X						
Ethyl methacrylate			X							X						X		X	
Ethyl methanesulfonate																X		X	
Ethyl nitrite			X							X									
Ethyl phosphonothioic dichloride			X							X	X	X							
Ethyl phosphorodichloridate			X							X									
Ethyl silicate			X							X									
Ethyl thiocyanate									X										
Ethyl toluene																			
Ethylaluminum dichloride			X							X									
Ethylaluminum sesquichloride			X							X									
Ethylamine	Y		X				X	X		X	X		X			X			

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Ethylbenzene	X	X	X	X	X	X	X	X		X		X	X			X	X		
Ethylbis(2-chloroethyl) amine									X						X				
Ethyl dichlorosilane			X							X	X								
Ethylene	X	X	X							X	X	X	X	X			X		
Ethylene chlorohydrin			X							X					X				
Ethylene cyanohydrin			X					X							X	X			
Ethylenediamine			X				X	X	X	X									
Ethylene dibromide	Z	X	X				X			X						X	X	X	
Ethylene dichloride	X	X	X	X		X	X			X		X				X	X	X	
Ethylene fluorohydrin									X										X
Ethylene glycol	X	X	X					X				X	X				X		
Ethylene glycol diacetate			X																
Ethylene glycol diethyl ether			X							X									
Ethylene glycol dimethyl ether			X																
Ethylene glycol monobutyl ether	Z		X							X									
Ethylene glycol monobutyl ether acetate			X																
Ethylene glycol monoethyl ether			X				X			X							X		
Ethylene glycol monoethyl ether acetate			X							X									
Ethylene glycol monomethyl ether			X							X							X		
Ethylene oxide	X	X	X			X			X	X	X	X		X	X	X	X	X	
Ethylene tetrachloride																			
Ethylene thiourea	Z																		
Ethylenediamine tetraacetic acid			X				X			X						X			
Ethyleneimine	Z		X						X	X	X				X	X	X	X	
Ethylhexaldehyde			X																
Ethylhexanol	X		X									X	X						
Ethylhexoic acid																			
Ethylhexylacrylate			X																
Ethylidenenorbornene			X																
Ethylmercuric phosphate									X						X				
Ethylphenyldichlorosilane			X							X									
Ethylpropylacrolein			X																
Ethyltrichlorosilane			X							X									
Famphur																X		X	
Fenitrothion	X	X							X				X		X				
Fensulfothion	Z								X						X				
Ferric ammonium citrate			X				X			X						X			
Ferric ammonium oxalate			X				X			X						X			
Ferric chloride	X	X	X			X	X	X		X			X	X		X			
Ferric fluoride							X			X									
Ferric glycerophosphate			X																
Ferric hydroxide	Z												X						
Ferric nitrate			X				X			X									
Ferric oxide	Y												X						
Ferric sulfate			X				X			X			X						
Ferrous ammonium sulfate			X				X			X									
Ferrous chloride			X				X			X						X			
Ferrous fluoroborate			X																
Ferrous oxalate			X																
Ferrous sulfate	Y		X				X	X		X			X			X			
Flampropmethyl	Y												X						
Fluenetil									X						X				
Fluoboric acid										X			X						
Fluometuron	Z																X		
Fluoranthene	Z			X	X		X												
Fluorene				X			X									X			
Fluorine	Z		X						X	X	X				X	X		X	
Fluoroacetamide	Z														X	X		X	
Fluoroacetic acid	Z									X					X				
Fluoroacetyl chloride															X				

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Fluorouracil															X				
Fluosilicic acid						X				X									
Fluosulfonic acid			X							X									
Fenophos	Y								X						X				
Formaldehyde	X	X	X			X	X	X	X	X		X	X	X	X	X	X	X	
Formaldehyde cyanohydrin									X						X				
Formic acid	X	X	X				X			X						X		X	
Formothion									X										
Fumaric acid	Z		X				X			X			X			X			
Furan									X	X									
Furazolidone	Z																		
Furfural	Z		X				X	X		X									
Furfuryl alcohol	Z		X							X									
Gallic acid			X																
Gas oil, cracked			X																
Gasolines			X							X				X					
Glutamic acid																			
Glutaraldehyde solution			X																
Glycerine	Z		X					X				X							
Glycidyl methyacrylate	Z		X																
Glycidylaldehyde																X		X	
Glyoxal			X																
Glyphosate	Y												X						
Heavy water	Y												X						
Heptachlor			X	X	X		X			X						X	X	X	
Heptachloroperoxide				X												X			
Heptane			X							X									
Heptanol	Z		X																
Heptene			X							X									
Herbadox																			
Herban																			
Herbisan																			
Hexachlorobenzene	Z			X						X						X	X	X	X
Hexachlorobutadiene	Y			X	X					X							X		
Hexachlorocyclopentadiene	Z		X	X	X		X		X	X					X	X	X	X	
Hexachloroethane	Z		X							X						X	X	X	
Hexachloronaphthalene									X						X		X		
Hexachlorophene	Y						X			X						X		X	
Hexachloropropene																			
Hexadecyltrimethylammonium chloride			X																
Hexaethyl tetraphosphate	Z									X	X					X		X	
Hexaldehyde	Z		X							X									
Hexamethylenediamine			X							X		X		X					
Hexamethylenetetramine			X																
Hexamethyleneimine			X							X									
Hexamethylphosphoramide																	X		
Hexane	Z	X	X					X		X		X	X						
Hexanol	Z		X							X									
Hexene			X							X									
Hexylene glycol			X																
Hydrazine	X	X	X						X	X	X		X		X	X	X	X	
Hydrochloric acid	X	X	X			X	X	X	X	X	X	X	X	X	X	X	X		
Hydrocyanic acid	Y		X				X	X	X	X	X	X		X	X	X	X	X	
Hydrofluoric acid	X	X	X			X	X	X	X	X	X		X	X	X	X	X	X	
Hydrogen	Z	X	X							X	X								
Hydrogen bromide			X							X	X								
Hydrogen peroxide	X	X	X			X		X	X	X	X		X	X	X				
Hydrogen selenide									X	X	X				X				
Hydrogen sulfide	Y	X	X				X		X	X	X				X	X		X	
Hydroquinone	Y		X						X	X					X		X		

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Hydroxyacetic acid																			
Hydroxylamine sulfate			X							X									
Hydroxypropyl acrylate			X																
Hydroxypropyl methacrylate			X																
Indeno(1,2,3-cd)pyrene																			
Iodine																			
Iodomethane	Z														X	X	X	X	
Iridium 192													X						
Isoamyl acetate																			
Isoamyl alcohol			X																
Isoamyl nitrate																			
Isobenzan	Z								X										
Isobutane			X							X	X								
Isobutyl acetate			X			X				X						X			
Isobutyl acrylate	Z									X									
Isobutyl alcohol	Z		X							X						X		X	
Isobutylamine			X			X				X						X			
Isobutylene			X							X	X	X							
Isobutyraldehyde										X							X		
Isobutyric acid			X							X						X			
Isobutyronitrile			X						X	X					X				
Isodecaldehyde			X																
Isodecyl acrylate			X																
Isodecyl alcohol			X																
Isodrin	V								X										
Isooctaldehyde			X																
Isooctyl alcohol	Z		X																
Isopentane			X							X									
Isophorone	Z		X	X	X											X			
Isophorone diisocyanate									X	X					X				
Isophthalic acid			X																
Isoprene			X				X			X						X			
Isopropanolamine			X																
Isopropanolamine dodecylbenzenesulfonate							X			X									
Isopropyl acetate			X							X									
Isopropyl alcohol	X	X	X						X	X		X	X	X			X		
Isopropyl chloroformate									X	X					X				
Isopropyl ether			X																
Isopropyl formate									X										
Isopropyl mercaptan			X							X									
Isopropyl percarbonate			X																
Isopropylamine			X							X									
Isopropylamine dodecylbenzenesulfonate		X																	
Isopropylmethylpyrazoyl dimethylcarb	Z														X				
Isovaleraldehyde	Z		X																
Jet fuel, JP-1			X																
Jet fuel, JP-3			X																
Jet fuel, JP-4			X																
Jet fuel, JP-5			X																
Kelthane							X			X						X	X		
Kepone	V						X			X						X		X	
Kerosene			X							X									
Lactic acid			X																
Lactonitrile	Z								X						X				
Lauric acid																			
Lauroyl peroxide			X							X									
Lauryl alcohol			X																
Lauryl mercaptan			X																
Lead				X	X		X									X	X	X	
Lead acetate			X		X		X			X						X		X	

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Lead arsenate	Z		X		X		X			X						X			
Lead chloride	Z				X		X			X						X			
Lead chromate		X			X														
Lead dioxide					X					X									
Lead fluoride			X		X		X			X						X			
Lead fluoroborate	Z		X		X		X			X									
Lead iodide			X		X		X			X									
Lead nitrate			X		X		X			X									
Lead oxide	X	X	X		X					X			X						
Lead phosphate					X											X		X	
Lead stearate					X		X			X						X			
Lead sulfate					X		X			X						X			
Lead sulfide					X		X			X						X			
Lead tetraacetate			X		X														
Lead thiocyanate			X		X		X			X						X			
Lewisite									X						X				
Lignin sulfonate	X												X						
Lithium			X							X									
Lithium aluminum hydride			X							X									
Lithium bromide	Z												X						
Lithium carbonate																			
Lithium chromate							X			X									
Lithium hydride			X						X	X					X				
Magnesium			X							X									
Magnesium chloride										X									
Magnesium hydroxide	Y	X											X						
Magnesium oxide	Z												X						
Magnesium perchlorate			X							X									
Magnesium sulfate																			
Malathion	X	X	X				X	X		X			X			X			
Maleic acid	Z		X				X	X		X						X			
Maleic anhydride	X	X	X				X	X		X		X				X	X	X	
Maleic hydrazide			X													X		X	
Malononitrile	Z								X	X					X	X		X	
Maneb	X									X			X						
Mannitol										X									
MCPA	X	X											X						
MCPB																			
Melamine	Z																X		
Mephosfolan	Z								X						X				
Mercaptobenzothiazole																			
Mercaptodimethur							X			X									
Mercuric acetate	Y		X		X				X	X					X				
Mercuric ammonium chloride			X		X					X									
Mercuric chloride	Y		X		X				X	X					X				
Mercuric cyanide			X		X		X			X	X					X			
Mercuric iodide			X		X					X									
Mercuric nitrate			X		X		X			X									
Mercuric oxide			X		X				X	X									
Mercuric sulfate					X		X			X						X			
Mercuric sulfide	Z		X		X								X						
Mercuric thiocyanate	Y				X		X			X									
Mercurous chloride			X		X														
Mercurous nitrate	Y		X		X		X			X						X			
Mercury	X	X	X	X	X					X			X			X	X	X	
Mercury fulminate					X		X			X						X		X	
Mesityl oxide			X							X									
Mesitylene									X						X				
Methacrylamide																			
Methyacrylicanhydride									X						X				

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Methacrylonitrile									X						X	X		X	
Methacryloyl chloride									X										
Methallyl chloride			X							X									
Methane			X							X	X								
Methanesulfonyl fluoride	Z														X				
Methidathion									X						X				
Methiocarb	Y								X						X	X			
Methionine																			
Methoxychlor	X		X				X			X			X			X	X	X	
Methoxyethylmercuric acetate									X						X				
Methyl 2-chloroacrylate	Y								X						X				
Methyl acetate			X							X									
Methyl acetylenepropadiene mixture			X							X	X								
Methyl acrylate			X					X		X							X		
Methyl alcohol	X	X	X			X		X	X	X		X	X	X		X	X	X	
Methyl amyl acetate																			
Methyl amyl alcohol	Z		X																
2-Methyl benzenamine hydrochloride																			
Methyl bromide	Z		X	X					X	X	X				X	X	X	X	
Methyl butyl ether										X							X		
Methyl butyl ketone			X																
Methyl chloride	X		X	X		X	X	X		X	X	X	X	X		X	X	X	
Methyl chloroformate			X						X	X					X	X		X	
Methyl disulfide									X						X				
Methyl ethyl ketone	X	X	X			X		X		X		X	X	X		X	X	X	
Methyl ethyl ketone peroxide	Z									X	X		X			X		X	
Methyl ethyl phenol methyl carbamate																			
Methyl ethyl pyridine			X							X									
Methyl formate			X							X									
Methyl hexyl ketone	X												X						
Methyl hydrazine			X						X	X					X	X	X	X	
Methyl isobutyl carbinol			X							X									
Methyl isobutyl ketone	Z	X	X					X		X						X	X	X	
Methyl isocyanate									X	X					X	X	X	X	
Methyl isopropenyl ketone			X							X									
Methyl mercaptan			X				X		X	X	X				X	X		X	
Methyl methacrylate	X	X	X			X	X	X		X		X	X	X		X	X	X	X
Methyl parathion	Y		X				X	X		X					X	X		X	
Methyl phenkapton	Z							X							X				
Methyl phosphonothioic dichloride			X						X	X									
Methyl salicylate																			
Methyl thiocyanate									X						X				
Methyl thiochlorosilane																			
Methyl vinyl ketone			X						X	X									
2-Methyl-5-vinyl pyridine									X						X				
Methylacetylene																			
Methylamine	X	X	X			X	X			X	X		X			X			
Methylaniline			X							X									
Methylcyclopentane			X							X									
Methylcyclopentadienyl manganese tricarbonyl			X																
Methyldichlorosilane			X							X	X								
Methylene chloride	X	X	X	X				X		X		X	X			X	X	X	X
4,4'-Methylene dianiline																			
1,2-Methylenedioxy-4-allylbenzene																			
1,2-Methylenedioxy-4-propenylbenzene																X		X	
1,2-Methylenedioxy4-propylbenzene																X		X	
Methylethanolamine																			
Methylmercuric dicyanamide									X						X				
Methyl pyrrolidone			X																
Methylstyrene	Z		X																

TABLE A4 — LISTS OF PRIORITY SUBSTANCES

A = 1980 PRIORITY LIST
B = 1981 PRIORITY LIST
C = U.S. COAST GUARD CHRIS LIST
D = EPA PRIORITY LIST
E = OLD EPA PRIORITY LIST
F = US RAILROAD SPILL LIST
G = US REPORTABLE QUANTITIES
H = US COAST GUARD SPILL LIST
I = EPA EXTREME DANGER LIST
J = TDG SCHEDULE 2
K = TDG SCHEDULE 12
L = US. TOP 100 CHEMICALS
M = CHEMICALS SPILLED IN CANADA
N = AAR HAZARDOUS LIST
O = SARA LIST OF EXTREMELY HAZARDOUS
P = CERCLA HAZARDOUS SUBSTANCES
R = RCRA HAZARDOUS LIST
S = CEPA PRIORITY SUBSTANCES
Q = SARA SECTION 313
X = TOP 100 MEMBERSHIP, Y = TOP 200, Z = TOP 500

SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Methylthiouracil			X																
Methyltrichlorosilane									X	X									
Methomyl									X										
Metobromuron	Z																		
Metolcarb									X						X				
Mevinphos	Y						X		X	X	X				X	X		X	
Mexacarbate	Z						X		X	X					X	X		X	
Mineral spirits			X																
Molybdenum trioxide			X														X		
Monocrotophos	Z								X						X				
Morpholine	Z	X	X							X									
MTBA																			
MTBE																			X
Nabam			X																
Naled	Y						X	X		X						X			
Naphtha	Z	X	X			X				X									
Naphthalene	X		X	X	X		X	X		X		X	X			X	X	X	
1,4-Naphthalenedione																X		X	
Naphthenic acids			X				X			X						X			
Naphthol	Z																		
Naphthylamine			X							X						X	X	X	
Natural gas		X	X							X	X								
Neohexane			X							X									
Neopentyl glycol	Z												X						
Nickel				X	X				X						X	X	X		X
Nickel acetate			X		X														X
Nickel ammonium sulfate			X		X					X									X
Nickel bromide			X		X														X
Nickel carbonyl	Y		X		X				X	X	X		X						X
Nickel chloride	Z		X		X					X						X			X
Nickel cyanide			X		X					X						X		X	X
Nickel fluoroborate			X		X														X
Nickel formate			X		X														X
Nickel hydroxide					X		X			X									
Nickel nitrate			X		X		X			X									X
Nickel sulfate	Z		X		X		X			X						X			X
Nicotine			X						X	X					X	X		X	
Nicotine sulfate			X						X	X					X				
Nitralin	Z		X										X						
Nitric acid	X	X	X			X	X	X	X	X	X	X	X		X	X	X		
Nitric oxide			X						X	X	X								
Nitrilotriacetic acid	Z	X	X														X		
Nitrites										X									
Nitroanilines	X		X							X			X						
Nitrobenzene	Z		X	X	X		X	X	X	X		X			X	X	X	X	
Nitroethane			X							X									
Nitrofen																X			
Nitrogen	X		X							X		X	X						
Nitrogen dioxide	Y						X	X	X	X	X		X						
Nitrogen tetroxide			X							X	X								
Nitroglycerin	Z	X								X						X	X	X	
Nitromethane	Z		X							X									
Nitrophenols	Z		X	X	X		X			X						X			
Nitropropane	Z		X							X						X	X	X	
N-Nitrosodimethylamine	Z			X	X				X							X	X		
p-Nitrosodiphenylamine	Z				X											X	X		
Nitrosoguanidine										X	X								
Nitrosyl chloride			X							X	X								
Nitrotoluenes	Z						X			X						X			
Nitrous oxide	Y		X							X			X						

TABLE A4 — LISTS OF PRIORITY SUBSTANCES

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F = US RAILROAD SPILL LIST
G = US REPORTABLE QUANTITIES
H = US COAST GUARD SPILL LIST
I = EPA EXTREME DANGER LIST
J = TDG SCHEDULE 2
K = TDG SCHEDULE 12
L = US. TOP 100 CHEMICALS
M = CHEMICALS SPILLED IN CANADA
N = AAR HAZARDOUS LIST
O = SARA LIST OF EXTREMELY HAZARDOUS
P = CERCLA HAZARDOUS SUBSTANCES
R = RCRA HAZARDOUS LIST
S = CEPA PRIORITY SUBSTANCES
Q = SARA SECTION 313
X = TOP 100 MEMBERSHIP, Y = TOP 200, Z = TOP 500

SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Nonane	Z		X							X			X						
Nonanoic acid																			
Nonanol	Z		X																
Nonene			X									X							
Nonylphenol	X	X	X										X						
Norbormide									X						X				
Octachloronaphthalene																	X		
Octamethyl pyrophosphoramide															X	X		X	
Octane			X							X									
Octanol	Z		X					X											
Octene			X																
Octyl aldehyde										X									
Octyl epoxy tallate			X																
Oils, croton			X																
Oils, fuel: 2			X											X					
Oils, fuel: 6			X																
Oleic acid	Z		X																
Oleum	Z		X							X	X								
Oxalic acid	Z		X																
1,2-Oxathiolane-2,2-dioxide																X	X	X	
10,10'-Oxydiphenoxarsine															X				
Oxydisulfoton									X						X				
Oxygen	X		X							X	X	X	X						
Paraldehyde										X						X			
Paraquat	X								X				X		X				
Paraquat dimethylsulfate																			
Parathion	X		X				X	X	X	X	X		X		X	X	X	X	
PCBs	X	X	X	X	X		X	X		X			X			X	X		
Pentaborane			X						X	X									
Pentachlorobenzene	Z						X									X		X	
Pentachloroethane							X		X	X					X	X		X	
Pentachloronitrobenzene																X	X	X	
Pentachlorophenol	X	X	X	X	X		X	X	X	X			X		X	X	X	X	
Pentadecanol			X																
Pentadecylamine									X						X				
Pentaerythritol		X	X																
Pentane			X							X									
Pentene			X																
Peracetic acid			X						X	X					X		X		
Perchloric acid			X							X									
Perchloroethylene	X		X	X	X			X		X		X	X						X
Perchloromethyl mercaptan									X	X					X	X		X	
Petroleum naphtha			X							X									
Phenanthrene	Z			X			X									X			
Phenol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Phenolsulfonic acid	Y												X						
Phenyl hydrazine hydrochloride			X						X						X				
Phenyl mercuric acetate	Y						X		X	X			X		X	X		X	
Phenyldichloroarsine			X						X	X					X	X		X	
p-Phenylenediamine	Z																X		
2-Phenylphenol																	X		
Phenylsilatrane									X						X				
Phenylthiourea	Z								X						X	X		X	
Phorate	Z						X		X						X	X		X	
Phosacetim									X						X				
Phosfolan									X						X				
Phosgene	Z		X			X	X		X	X	X	X	X		X	X	X	X	
Phosmet	Z								X						X				
Phosphamidon	X								X				X						
Phosphine	Z								X	X	X		X		X	X		X	

TABLE A4 LISTS OF PRIORITY SUBSTANCES

A = 1990 PRIORITY LIST	B = 1991 PRIORITY LIST	C = U.S. COAST GUARD CHRIS LIST
D = EPA PRIORITY LIST	E = OLD EPA PRIORITY LIST	F = US RAILROAD SPILL LIST
G = US REPORTABLE QUANTITIES	H = US COAST GUARD SPILL LIST	I = EPA EXTREME DANGER LIST
J = TDG SCHEDULE 2	K = TDG SCHEDULE 12	L = US. TOP 100 CHEMICALS
M = CHEMICALS SPILLED IN CANADA	N = AAR HAZARDOUS LIST	O = SARA LIST OF EXTREMELY HAZARDOUS
P = CERCLA HAZARDOUS SUBSTANCES	R = RCRA HAZARDOUS LIST	S = CEPA PRIORITY SUBSTANCES
Q = SARA SECTION 313	X = TOP 100 MEMBERSHIP, Y = TOP 250, Z = TOP 500	

SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Phosphoric acid	X	X	X			X	X	X		X		X	X	X		X	X		
Phosphorus	X	X	X			X	X	X	X	X		X	X		X	X	X		
Phosphorus oxychloride			X			X	X	X	X	X									
Phosphorus pentasulfide			X				X			X						X		X	
Phosphorus pentoxide	Y								X	X			X		X	X	X		
Phosphorus, red			X							X									
Phosphorus tribromide			X							X									
Phosphorus trichloride			X			X	X		X	X					X	X			
Phosphorus, white			X							X	X			X					
Phthalic acid																			
Phthalic anhydride	X	X	X							X		X	X			X	X	X	
Picloram	X												X						
2-Picoline										X						X		X	
Picric acid										X	X						X		
Piperazine			X							X									
Piperidine									X	X					X				
Polyaromatic hydrocarbons																			X
Polyphosphoric acid			X																
Polypropylene			X																
Potassium			X							X									
Potassium aluminate	Z																		
Potassium arsenate			X				X	X		X									
Potassium arsenite							X		X	X									
Potassium binoxalate			X																
Potassium bromate										X									
Potassium carbonate	Y												X						
Potassium chlorate	Z		X							X									
Potassium chloride	X	X											X						
Potassium chromate			X				X	X		X						X			
Potassium cyanide	X		X				X	X	X	X	X		X		X	X		X	
Potassium dichloroisocyanurate			X							X									
Potassium dichromate	Z		X				X			X						X			
Potassium fluoride										X									
Potassium hydroxide	X	X	X			X	X	X		X		X	X	X		X			
Potassium iodide			X																
Potassium metabisulfite										X									
Potassium nitrate						X				X				X					
Potassium oxalate			X																
Potassium permanganate	X		X			X	X	X		X			X			X			
Potassium peroxide			X							X									
Potassium phosphide										X	X								
Potassium silver cyanide									X						X	X		X	
Potassium sorbate																			
Potassium sulfate	Z	X																	
Promecarb									X						X				
Propane			X							X	X								
Propanolamine																			
Propargite							X			X						X			
Propargyl alcohol	Y									X						X		X	
Propargyl bromide									X						X				
Propiolactone			X						X						X		X		
Propionaldehyde	Z		X							X							X		
Propionic acids	X		X				X	X		X			X			X			
Propionic anhydride	Z		X				X			X						X			
Propionitrile									X	X					X	X		X	
Propoxur																	X		
Propyl acetate			X							X									
Propyl alcohol			X					X		X									
Propyl chloroformate									X	X					X				
Propyl mercaptan			X							X									

TABLE A4 LISTS OF PRIORITY SUBSTANCES

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E = OLD EPA PRIORITY LIST
F = US RAILROAD SPILL LIST
G = US REPORTABLE QUANTITIES
H = US COAST GUARD SPILL LIST
I = EPA EXTREME DANGER LIST
J = TDG SCHEDULE 3
K = TDG SCHEDULE 12
L = US. TOP 100 CHEMICALS
M = CHEMICALS SPILLED IN CANADA
N = AAR HAZARDOUS LIST
O = SARA LIST OF EXTREMELY HAZARDOUS
P = CERCLA HAZARDOUS SUBSTANCES
Q = RCRA HAZARDOUS LIST
R = CEPA PRIORITY SUBSTANCES
S = SARA SECTION 313
X = TOP 100 MEMBERSHIP, Y = TOP 250, Z = TOP 500

SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Propylamine	Z		X							X									
Propylene	X	X	X							X	X	X	X				X		
Propylene chlorohydrin	Z									X			X						
Propylene glycol	X	X	X									X	X						
Propylene glycol allyl ether															X				
Propylene glycol methyl ether			X																
Propylene oxide	X	X	X			X	X	X	X	X	X	X	X	X	X	X	X		
Propyleneimine			X						X	X					X	X	X	X	
Prothoate															X				
Pseudocumene															X	X			
Pyrene				X			X		X						X	X			
Pyrethrins							X			X					X				
Pyridine	X		X			X	X			X			X						
Pyrocatechol	Z																		
Pyrogallic acid			X																
Quinoline	Z		X				X			X						X	X		
Quinone	Z																		
Resorcinol	Z		X				X	X		X						X		X	
Rotenone	Y																		
Salicylic acid	Z		X																
Sarin									X						X				
Selenious acid							X		X						X	X		X	
Selenium				X	X		X												
Selenium dioxide			X				X									X		X	
Selenium disulfide										X						X		X	
Selenium oxychloride									X						X				
Selenium trioxide			X																
Semicarbazide hydrochloride									X						X				
Silicon tetrachloride			X							X									
Silver				X	X											X	X	X	
Silver acetate			X		X														
Silver carbonate			X		X														
Silver fluoride			X		X														
Silver iodate			X		X														
Silver nitrate	Z		X		X		X			X						X			
Silver oxide			X		X														
Silver sulfate			X		X														
Sodium	Z		X				X	X		X			X	X		X			
Sodium acetate																			
Sodium aluminate	Y	X								X			X						
Sodium amide			X							X									
Sodium anthraquinone sulfonate	Z								X						X				
Sodium arsenate	Z		X				X		X	X					X	X			
Sodium arsenite	Y	X	X				X	X	X	X			X		X	X			
Sodium azide	Y		X						X	X									
Sodium benzoate																			
Sodium bicarbonate																			
Sodium bifluoride							X			X									
Sodium bisulfate						X				X									
Sodium bisulfite	Z	X	X			X	X			X						X			
Sodium borate	Y	X	X																
Sodium borohydride	Y	X	X							X			X						
Sodium borohydrite																			
Sodium bromide																			
Sodium cacodylate			X						X	X					X				
Sodium carbonate	X	X										X	X						
Sodium chlorate	X	X	X							X		X	X	X					
Sodium chloride	X	X											X						
Sodium chlorite										X									
Sodium chromate	Y		X				X			X			X			X			

TABLE A4 — LISTS OF PRIORITY SUBSTANCES

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E = OLD EPA PRIORITY LIST
F = US RAILROAD SPILL LIST
G = US REPORTABLE QUANTITIES
H = US COAST GUARD SPILL LIST
I = EPA EXTREME DANGER LIST
J = TDG SCHEDULE 2
K = TDG SCHEDULE 12
L = US. TOP 100 CHEMICALS
M = CHEMICALS SPILLED IN CANADA
N = AAR HAZARDOUS LIST
O = SARA LIST OF EXTREMELY HAZARDOUS
P = CERCLA HAZARDOUS SUBSTANCES
R = RCRA HAZARDOUS LIST
S = CEPA PRIORITY SUBSTANCES
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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Sodium cyanide	X	X	X			X	X	X	X	X	X		X		X	X		X	
Sodium dichloroisocyanurate			X							X									
Sodium dichromate	Y	X	X				X	X		X									
Sodium ferrocyanide			X																
Sodium fluoride	X		X				X			X			X			X			
Sodium fluoroacetate	Z								X	X						X		X	
Sodium fluoroaluminate																			
Sodium fluorosilicate	Z									X									
Sodium formate																			
Sodium hydride			X							X									
Sodium hydrosulfide	Z		X				X	X		X	X		X						
Sodium hydrosulfite	X																		
Sodium hydroxide	X	X	X			X	X	X		X		X	X	X		X	X		
Sodium hypochlorite	X	X	X				X						X			X			
Sodium methanearsonate			X																
Sodium methylate			X				X			X						X			
Sodium nitrate	Y					X		X		X			X	X					
Sodium nitrite			X				X			X						X			
Sodium oxalate			X																
Sodium pentachlorophenate									X	X					X				
Sodium perchlorate										X									
Sodium phosphate, dibasic	Y	X	X				X	X		X						X			
Sodium phosphate, monobasic	Y	X	X					X											
Sodium phosphate, tribasic	Z	X	X				X	X		X						X			
Sodium phosphide										X	X								
Sodium selenite	Z						X		X	X						X			
Sodium silicate	X	X	X									X	X						
Sodium sulfate	Z	X										X					X		
Sodium sulfide			X					X		X									
Sodium sulfite	X	X	X										X						
Sodium thiocyanate			X																
Sodium thioglycolate	Z												X						
Sodium thiosulfate pentahydrate																			
Sodium tripolyphosphate												X							
Sorbic acid																			
Sorbitol			X																
Stannic chloride	Z									X			X						
Stannous chloride	Z									X									
Strontium										X									
Strontium chromate							X			X									
Strontium nitrate										X									
Strontium sulfide																X			
Strychnine	Y						X	X	X	X	X				X	X		X	
Strychnine sulfate	Z								X	X	X				X				
Styrene	X	X	X			X	X	X		X		X	X	X		X	X		X
Styrene oxide																	X		
Sulfamic acid	Z									X									
Sulfolane			X																
Sulfotep	Z								X						X	X		X	
Sulfur	X	X	X					X		X			X						
Sulfur chloride	Z		X				X	X		X			X						
Sulfur dioxide	X	X	X						X	X	X		X	X	X				
Sulfur tetrafluoride									X	X	X				X				
Sulfur trioxide									X	X	X				X				
Sulfuric acid	X	X	X			X	X	X	X	X	X	X	X	X	X	X	X		
Sulfuryl chloride	Z	X	X							X			X						
Sulfuryl fluoride										X	X		X						
2,4,5-T			X				X			X						X		X	
2,4,5-T amines							X			X						X			
2,4,5-T esters			X				X			X						X			

TABLE A4 LISTS OF PRIORITY SUBSTANCES

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F = US RAILROAD SPILL LIST
G = US REPORTABLE QUANTITIES
H = US COAST GUARD SPILL LIST
I = EPA EXTREME DANGER LIST
J = TDG SCHEDULE 2
K = TDG SCHEDULE 12
L = US. TOP 100 CHEMICALS
M = CHEMICALS SPILLED IN CANADA
N = AAR HAZARDOUS LIST
O = SARA LIST OF EXTREMELY HAZARDOUS
P = CERCLA HAZARDOUS SUBSTANCES
R = RCRA HAZARDOUS LIST
S = CEPA PRIORITY SUBSTANCES
Q = SARA SECTION 313
X = TOP 100 MEMBERSHIP, Y = TOP 200, Z = TOP 500

SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
2,4,5-T salts							X			X						X			
Tabun									X						X				
Tall oil		X																	
Tannic acid			X																
Tartaric acid																			
Tebuthiuron																			
Tellurium hexafluoride									X	X	X				X				
Temephos	Z																		
Terephthalic acid	X	X										X	X				X		
Terphenyl	Z	X											X						
Tetrabutyl titanate			X																
1,2,4,5-Tetrachlorobenzene																X		X	X
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)				X	X					X						X			
Tetrachloroethane	X		X	X						X						X	X	X	X
2,3,4,6-Tetrachlorophenol																X		X	
Tetrachlorvinphos																	X		
Tetradecanol			X																
Tetradecene			X																
Tetradecylbenzene			X																
Tetraethyl lead	X	X	X			X	X	X	X	X	X		X		X	X		X	
Tetraethyl pyrophosphate (TEPP)	Y		X				X			X	X				X	X		X	
Tetraethylene glycol			X																
Tetraethylenepentamine			X							X									
Tetraethyltin															X				
Tetrafluoroethylene			X							X	X								
Tetrahydrofuran			X			X				X						X		X	
Tetrahydronaphthalene	Z		X										X						
Tetramethyllead	Z		X						X						Y				
Tetranitromethane										X	X				X	X		X	
Tetrasodium pyrophosphate																			
Thallic peroxide																			
Thallium	Z			X	X		X			X						X	X		
Thallium acetate	Z				X		X			X						X		X	
Thallium carbonate					X		X			X					X	X		X	
Thallium chloride					X		X			X					X	X		X	
Thallium nitrate					X		X			X									
Thallium peroxide					X		X			X					X	X		X	
Thallium selenide					X		X			X									
Thallium sulfate	Z				X		X		X	X			X						
Thioglycolic acid	X								X				X						
Thiometon									X						X				
Thionazin									X						X	X		X	
2,2'-Thiobis(4,6-dichlorophenol)															X				
2,2'-Thiobis(4-chloro-6-methylphenol)															X				
Thionyl chloride	Z									X			X						
Thiophan sulfone																			
Thiophenol									X						X	X		X	
Thiophosgene			X							X	X								
Thiosemicarbazide	Z								X						X	X		X	
Thiourea	Z									X									
Thiram	Y									X			X						
Thorium dioxide																	X		
Thorium nitrate			X							X									
Thyroxine																			
Titanium dioxide	X	X										X	X						
Titanium tetrachloride			X							X					X		X		
Toluene	X	X	X	X	X	X	X	X		X		X	X	X		X	X	X	X
Toluene-2,4-diamine	X									X			X			X	X	X	
Toluene-2,4-diisocyanate	X	X	X						X	X		X	X	X	X	X	X		
Toluene-2,6-diisocyanate									X	X		X			X	X	X		

TABLE A4

LISTS OF PRIORITY SUBSTANCES

A = 1990 PRIORITY LIST
B = 1991 PRIORITY LIST
C = U.S. COAST GUARD CHRIS LIST
D = EPA PRIORITY LIST
E = OLD EPA PRIORITY LIST
F = US RAILROAD SPILL LIST
G = US REPORTABLE QUANTITIES
H = US COAST GUARD SPILL LIST
I = EPA EXTREME DANGER LIST
J = TDG SCHEDULE 2
K = TDG SCHEDULE 12
L = US. TOP 100 CHEMICALS
M = CHEMICALS SPILLED IN CANADA
N = AAR HAZARDOUS LIST
O = SARA LIST OF EXTREMELY HAZARDOUS
P = CERCLA HAZARDOUS SUBSTANCES
R = RCRA HAZARDOUS LIST
S = CEPA PRIORITY SUBSTANCES
Q = SARA SECTION 313
X = TOP 100 MEMBERSHIP, Y = TOP 250, Z = TOP 500

SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Toluenesulfonic acid			X							X									
Toluidine	Z		X				X			X									
Tolyl thiourea																			
Toxaphene	Y			X	X		X	X		X									
Tri(2-butoxyethyl) phosphate																			
Triallate		X																	
Triamiphos									X						X				
Tributyl phosphate	X												X						
Trichlorofon	X	X					X		X	X			X		X	X	X		
Trichloroacetaldehyde																X		X	
Trichloroacetyl chloride									X	X					X				
Trichlorobenzene	Z		X	X						X						X	X		X
Trichlorocyanuric acid																			
1,1,1-Trichloroethane	X	X	X	X				X		X		X	X						X
1,1,2-Trichloroethane	X		X	X				X					X			X	X	X	
Trichloroethyl amine																			
1,1,1-Trichloroethylene	X		X	X	X		X	X		X			X			X	X	X	X
Trichlorofluoromethane		X	X	X												X		X	
Trichloronate									X						X				
Trichlorophenol	Z		X	X			X			X						X	X	X	
Trichlorophenoxy propionic acid	Z									X						X		X	
Trichlorophenyl silane															X				
Trichlorosilane			X							X	X								
Trichloro-s-triazinetrione			X							X									
Trichlorotrifluoroethane																			
Tri-o-cresyl phosphate										X									
Tridecane			X																
Tridecyl alcohol	Z		X																
Triethanolamine	Y		X				X						X						
Triethoxysilane									X						X				
Triethylaluminum			X							X									
Triethylamine	Z		X			X	X			X						X			
Triethylbenzene			X																
Triethylene glycol			X																
Triethylenetetraamine			X							X									
Trifluorochloroethylene			X							X	X								
3-(Trifluoromethyl) benzenamine									X						X				
Trifluralin	X	X	X										X				X		
Triisobutylaluminum			X							X									
Trimellitic anhydride																			
Trimethylamine	Z		X				X			X	X		X			X			
2,4,6-Trimethyl aniline									X						X				
Trimethylchlorosilane			X						X	X					X				
Trimethylene bromide	Y												X						
Trimethylene chloride																			
Trinitrobenzene							X			X	X					X		X	
Trinitrotoluene	X	X								X	X		X						
Triphenyltin chloride									X						X				
Tripropylene glycol			X																
Tris(1-aziridinyl) phosphine oxide			X																
Trisodium nitrilotriacetate			X																
Turpentine	Z	X	X					X		X									
Undecanol			X																
Undecylbenzene			X																
Uranium dioxide	Z	X											X						
Uranium hexafluoride										X	X								
Uranyl acetate			X				X			X						X			
Uranyl nitrate	X		X				X			X			X						
Uranyl sulfate			X																
Urea	Y	X	X									X							

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SUBSTANCE	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Urea peroxide			X							X									
Urethan																			
Valeraldehyde	Z		X							X									
Vanadium oxytrichloride			X							X									
Vanadium pentoxide	Y		X				X		X	X					X	X		X	
Vanadyl sulfate			X				X			X									
Vinyl acetate	X	X	X			X	X	X	X	X		X	X	X	X	X	X		
Vinyl bromide	X	X	X	X	X	X					X					X			
Vinyl chloride										X	X	X	X	X		X	X	X	
Vinyl fluoride			X							X	X								
Vinyl methyl ether			X							X	X								
Vinyl styrene																			
Vinylnorbornene									X						X				
Vinyltrichlorosilane			X							X									
Warfarin	Z								X						X	X		X	
Xylene	X	X	X			X	X	X		X		X	X	X					X
Xylenol	Z		X				X	X		X						X			
2,6-Xylidine										X							X		
Zinc				X	X		X									X	X		
Zinc acetate	Z		X		X		X			X						X			
Zinc ammonium chloride			X		X		X			X									
Zinc arsenate			X		X					X									
Zinc borate			X		X		X			X						X			
Zinc bromide	Z		X		X		X			X			X			X			
Zinc carbonate					X		X			X						X			
Zinc chloride	X	X	X		X		X	X		X			X			X			
Zinc chromate			X		X														
Zinc cyanide	X				X		X			X			X			X		X	
Zinc fluoride					X		X			X						X			
Zinc fluoroborate			X		X														
Zinc formate					X		X			X						X			
Zinc hydrosulfite					X		X			X						X			
Zinc nitrate			X		X		X			X						X			
Zinc oxide	X	X			X								X						
Zinc phenolsulfonate			X				X			X						X			
Zinc phosphate	X												X						
Zinc phosphide			X				X		X	X	X				X	X	X		
Zinc silicofluoride			X				X			X									
Zinc stearate																			
Zinc sulfate	X	X	X				X			X			X						
Zirconium acetate			X																
Zirconium nitrate			X				X			X									
Zirconium oxychloride			X																
Zirconium potassium fluoride							X			X									
Zirconium sulfate			X				X			X									
Zirconium tetrachloride							X			X									

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Acenaphthene	0.67	1.7	1.73	41 **	
Acenaphthylene					
Acetaldehyde		53	30.9	12427 **	
Acetamide				> 10000 *	TLm: 13300 mosquito fish
Acetic acid		TLm:75	88		
Acetic anhydride					
Acetoacetanilide					
Acetone	5540	8300	7200	TLm:10 **	5000 goldfish *
Acetone cyanohydrin		0.57			
Acetone thiosemicarbazide					
Acetonitrile		1660	1640	> 100	TLm:1660 guppy
Acetophenone			162		
Acetoxytriphenyl stannane					
Acetyl bromide			40.6		
Acetyl chloride					
Acetyl peroxide					
Acetylacetone	71.6	74.3	1365	100 *	
Acetylene					TLm: 200 river trout (33hrs)
Acridine	10 (1.08 days)			3.1	2.82 daphnia pulex *
Acrolein	0.1	0.08 *	0.02		0.048 brown trout *
Acrylamide	0.4 (days 7)				130 harlequin fish
Acrylic acid					
Acrylonitrile		TLm: 11.8 s.	Lm: 14.3 h. w.		TLm: 33.5 guppy soft water
Acryloyl chloride					
Adipic acid		< 330 *	97		TLm: 775 guppy soft water
Adiponitrile		720	1930		
Alachlor	2.4 - 3.2				
Aldicarb	0.56				
Aldrin	0.036	0.013	0.028	0.028 **	28 daphnia pulex **
Allyl alcohol				0.325	1.0 goldfish *
Allyl amine					
Allyl bromide					
Allyl chloride		TLm: 42.3 s.	Lm: 19.8 s. w.		10.0 goldfish *
Allyl chloroformate					
Allyltrichlorosilane					
Aluminum (fume or dust)					
Aluminum chloride	0.56 *** *				
Aluminum fluoride					
Aluminum hydroxide					
Aluminum nitrate					
Aluminum oxide					
Aluminum phosphate					
Aluminum sulfate					
Aminocarb	13.57	4.7	8.5		
Aminoethylethanolamine					
Aminopterin					
Amiton					
Amitrole		100 **		30 **	
Ammonia	0.16 - 0.49	1.5	0.75 - 3.4	156 **	164 daphnia pulex **
Ammonium acetate					TLm: 238 mosquito fish
Ammonium benzo[illegible]					
Ammonium bicarb[illegible]ate	17.7				
Ammonium bisulfate					
Ammonium carbamate					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Ammonium carbonate			37 (S)		
Ammonium chlorate					
Ammonium chloride	26.147	0.748		13	
Ammonium chromate					
Ammonium citrate					
Ammonium dichromate					
Ammonium fluoborate			> 600 (S)		
Ammonium fluoride			364 (S)		75 grass shrimp
Ammonium formate					
Ammonium hydrogen fluoride					
Ammonium hydroxide					
Ammonium iodide					
Ammonium molybdate					
Ammonium nitrate					
Ammonium oleate					
Ammonium oxalate					
Ammonium pentaborate					
Ammonium perchlorate					
Ammonium persulfate				TLm:120 **	
Ammonium phosphate dibasic					
Ammonium phosphate hemibasic					
Ammonium phosphate monobasic					
Ammonium picrate		220 (S)			
Ammonium silicofluoride			28.7 (S)		
Ammonium stearate					
Ammonium sulfamate			> 600 (S)		
Ammonium sulfate	37.96			202	
Ammonium sulfide					
Ammonium sulfite				TLm: 203 (100hrs)	
Ammonium tartrate					
Ammonium thiocyanate					
Ammonium thiosulfate					
Ammonium vanadate					
Amyl acetate		650 (S)		210 *	
Amyl alcohol				4030 *	
Amyl chloride					
Amyl mercaptan					
Amyl methyl ketone			131		
Amyl nitrate					
Amyltrichlorosilane					
Aniline	20		134		
Anisidine					
Anisoyl chloride					
Anthracene		0.0036		0.02 (57.6 min)	
Antimony pentachloride					
Antimony pentafluoride					
Antimony potassium tartrate					
Antimony tribromide					
Antimony trichloride					
Antimony trifluoride					
Antimony trioxide		> 440	> 833	> 530 **	
Arsenic	0.95			3.8 **	1.8 daphnia pulex **
Arsenic acid				6.6 **	
Arsenic disulfide					
Arsenic pentoxide	28				

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Arsenic trichloride					
Arsenic trioxide	43.0 (6 days)		109		
Arsenic trisulfide					
Arsine					
Asbestos					
Atlox					
Atrazine	12.6	40.26		54 **	> 40 d. pulex 107.2 min.
Azinphosethyl	0.019	0.0011			0.0032 daphnia pulex **
Azinphosmethyl	0.0062	0.0081	0.093	0.0056 *	0.013 perch
Barban					
Barium	42.7 *** *			410 **	
Barium carbonate					
Barium chlorate					
Barium chloride					
Barium cyanide					
Barium nitrate					
Barium perchlorate					
Barium permanganate					
Barium peroxide					
Barium sulfate	76000				
Benazolin					
Benzaldehyde	11.2	1.07	10.2	50 *	
Benzamide			661		
Benzene	6.6	61.245	5.3	429.75 **	15 daphnia pulex
Benzene hexachloride	0.08	0.062	0.087	0.460 **	0.460 daphnia pulex **
Benzenearsonic acid					
Benzenephosphorus dichloride					
Benzenephosphorus thiodichloride					
Benzenesulfonyl chloride					3.0 brown trout **
Benzidine				1540 *	
Benzoic acid			484		TLm: 180 mosquito fish
Benzonitrile		78	Lm: 135 s.	200 *	
Benzophenone			14.75		
Benzotrichloride					
Benzotrifluoride					
Benzoyl chloride			34.1		180 grass shrimp
Benzoyl peroxide					
Benzo(b)fluoranthene					
Benzo(ghi)perylene					
Benzo(j,k)fluorene					
Benzo(k)fluoranthene					
Benzyl alcohol		10	460		
Benzyl bromide					
Benzyl chloride			6		3.9 white shrimp
Benzyl chloroformate					
Benzyl cyanide					
Benzyl-n-butyl phthalate		43			
Benzylamine				TLm:60 **	
Benzyltrimethylammonium chloride					
Benz(a)anthracene					
Benz(a)acridine					0.440 daphnia pulex *
Beryllium					
Beryllium chloride				0.06	
Beryllium fluoride					
Beryllium nitrate				0.79 *	

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Beryllium oxide					
Beryllium sulfate					
Bismuth oxychloride					
Bisphenol A					
Bisphenol A diglycidyl ether					
Borax	78.5 * *				
Boric acid	100 * *			133 **	
Boron tribromide					
Boron trichloride					
Boron trifluoride		15000 *			
Bromine			16500	1.0 **	
Bromine pentafluoride					
Bromine trifluoride					
Bromoacetone					
Bromobenzene					
Bromochlorodifluoromethane					
Bromoform		29		46.0 **	44.0 daphnia pulex
Bromotrifluoromethane					
Bromoxynil					
Brucine		36			
BTX					
Butadiene					TLm: 71.5 pinperch *
Butane					
Butanediol					
Butenediol					
Butyl acetate		100	18	4730 *	
Butyl acrylate					
Butyl alcohol			1910 (S)	2802.5 *	
Butyl formate					
Butyl hydroperoxide					
Butyl isovalerate					
Butyl mercaptan		TLm: 5.5 **			
Butyl methacrylate					
Butyl peroxy-2-ethylhexanoate					
Butyl peroxypivalate					
Butyl phenol					
Butyl vinyl ether					
Butylamine	140	32	200	750 *	
Butylated hydroxytoluene					
Butylene					
Butylene oxide					
Butyltrichlorosilane					
Butyraldehyde			14.7	340 *	
Butyric acid		200 *		61.0 **	
Cacodylic acid					
Cadmium	0.0065			0.052 **	0.068 daphnia pulex **
Cadmium acetate					
Cadmium bromide					
Cadmium chloride	1.86	1.94		0.005	0.0387 daphnia pulex
Cadmium fluoroborate					
Cadmium nitrate	0.32 **			0.022 **	.065 daphnia pulex **
Cadmium oxide					
Cadmium stearate					
Cadmium sulfate	0.003			0.131 ***	
Calcium arsenate					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Calcium carbide					
Calcium carbonate					
Calcium chlorate					
Calcium chloride		3673		649 (100.8 hrs)	
Calcium chromate					
Calcium cyanamide					
Calcium cyanide		TLm:0.12			
Calcium fluoride					
Calcium formate					
Calcium hydroxide					
Calcium hypochlorite	0.07975	0.0623			
Calcium nitrate		2400			
Calcium oxide					
Calcium peroxide					
Calcium phosphate					
Calcium phosphide					
Calcium propionate					
Calcium resinate					
Calcium sulfate		2980			
Camphene				22.0 **	
Camphor oil			110 (S)		
Cantharidin					
Caprolactam					
Caprylic acid		Chemical too insoluble to be toxic			
Captan					0.3 harlequin fish (F)
Carbachol chloride					
Carbamidoselenic acid					
Carbaryl	4.3	6.8		.005 (63day	0.0064 daphnia pulex **
Carbofuran					
Carbon dioxide					TLm: 162-136 mosquito fish (24-96 h)
Carbon disulfide				2.1 **	
Carbon monoxide					
Carbon oxyfluoride					
Carbon tetrachloride	1.97	125	4	35.0 **	
Carbonyl sulfide					
Carbophenothion					
Carboxymethylcellulose	10000 (fry)				
Cesium 137					
Cetyl alcohol					
Chloramben					
Chlordane	0.0241	0.056	0.0369	0.153 **	0.029 daphnia pulex **
Chlorine	0.1666		0.082-0.095	0.120 **	0.069 daphnia pulex **
Chlorine dioxide					
Chlorine trifluoride					
Chlormequat					
Chloro nitrophenol					
Chloro nitrophenol, sodium salt					
Chloro phenyl phenol					
Chloro toluidine hydrochloride					
Chloro-dinitrophenol					
Chloro-m-cresol					
Chloroacetaldehyde					
Chloroacetic acid					
Chloroacetophenone					
Chloroacetyl chloride					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr, unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Chloroaniline	14	2.4	12		
Chlorobenzene	4.7	24	29	21.30 **	
Chlorobenzoyl peroxide					
Chlorobutyronitrile					
Chlorocyclopentylphenol					
Chlorodibromomethane					
Chlorodifluoroethane					
Chlorodifluoromethane					
Chloroethylvinyl ether		350			
Chloroform	2.06		> 98		102 guppy (14 days)
Chlorohydrin					
Chloromercuri dinitrophenol					
Chloromercuriphenol					
Chloromethyl methyl ether					
Chloronaphthalene				1.6 **	
Chloronitrobenzene		1.2 (S)	18.8		
Chloropentafluoroethane					
Chlorophacinone					
Chlorophenol	1.9	3.8	13.8		0.76 guppy *
Chlorophenol, potassium salt					
Chloropicrin					
Chloroprene					
Chlorosulfonic acid					
Chlorothalonil					
Chlorotoluidine					
Chlorotrifluoromethane					
Chloroxuron		25 **			
Chlorpropham		8.0 **			
Chlorpyrifos	0.0104	0.02		0.0004 *	0.12 0-3 daphnia pulex ***
Choline chloride					
Chromic acetate					
Chromic acid					
Chromic sulfate	750 (fry)			0.004 **	
Chromium	0.190 *** *			0.022 **	0.045 daphnia pulex **
Chromous chloride	11.2				
Chromyl chloride					
Cobalt					
Cobaltous acetate					
Cobaltous bromide	81.9 (S)				
Cobaltous chloride				1.6	
Cobaltous formate			32.2 (S)		
Cobaltous hydroxide					
Cobaltous nitrate	0.47 *** *			3.4 **	
Cobaltous sulfamate					
Cobaltous sulfate					
Copper acetate			0.39 (S)		
Copper acetoarsenite					
Copper arsenite					
Copper bromide					
Copper chloride	0.08	1.178		0.13	
Copper cyanide			1.2		
Copper hydroxide					
Copper iodide					
Copper naphthenate					
Copper nitrate		0.82			

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr, unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Copper oxalate					
Copper oxide					
Copper sulfate	0.224	1.1	0.075	0.02	0.020 daphnia pulex
Copper sulfate, ammoniated					
Copper tartrate					
Coumafuryl					
Coumaphos	1.5	0.18		0.0001 (1.08 days)	
Coumatetralyl					
Cresol	8.4	10.8	19		
Crimidine					
Crotonaldehyde		3.5			
Cumene	2.7			86 *	
Cumene hydroperoxide					
Cupferron					
Cyanoacetic acid					
Cyanogen					
Cyanogen bromide		0.24			
Cyanogen chloride					
Cyanogen iodide					
Cyanophos					14 harlequin fish ** (F)
Cyanuric acid					
Cyanuric fluoride					
Cyclohexene		34.72	93	340.0 *	
Cyclohexanol		1100	704		
Cyclohexanone			620.5	800.0 *	
Cyclohexanone peroxide					
Cyclohexenyl trichlorosilane					
Cycloheximide	1.4				
Cyclohexylamine					
Cyclopentane					
Cyclophosphamide					
Cyclopropane					
Cymene				6.5 **	
Dalapon		TLm 105			
DDD					0.0032 daphnia pulex **
DDE			BCF:51000 (32 days)		BCF:12037 mosquito fish (33 day
DDT	0.007	0.008	0.019	.00036 **	0.00036 daphnia pulex **
Decaborane					
Decabromodiphenyl oxide					
Decahydronaphthalene					
Decaldehyde					
Decane					
Decyl alcohol			2.4	1.8 *	
Decyl benzene					
Decyl octyl phthalate					
Demeton		0.11	3.2		
Demeton-S-methyl					
Di(p-chlorobenzoyl) peroxide					
Diacetone alcohol		420			
Diallate					
Diamyl phthalate					
Diazinon	1.35	0.44 - 0.48	6.8 - 10.0		0.0009 daphnia pulex **
Diazomethane					
Dibenzofuran			1.815	1.7 **	
Dibenz(a,h)anthracene					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Dibromomethane		18 **			
Dibutyl amine	21.25		31		
Dibutyl ether			32.3	26.0 **	
Dibutyl ketone					
Dicamba	28	> 50			
Dichlobenil	18	11.8		10 **	3.7 daphnia pulex **
Dichlone	0.048	0.148		0.025 **	0.028 daphnia pulex (1.04d)
Dichloro trichloromethyl benzhydrol					
Dichlorobenzene	1.58	27	0.76		
Dichlorobenzidine					
Dichlorobromomethane					
Dichlorodifluoroethane					
Dichlorodifluoromethane					
Dichloroethane	225	550	136	470.5 **	
Dichloroethoxy methane					
Dichloroethyl amino uracil					
Dichloroethyl ether		600 (S)			
Dichloroethylene		147	500	45.3 **	
Dichlorofluoromethane					
Dichloroisopropyl ether					
Dichloromethyl ether					
Dichloromethyl ketone					
Dichlorotetrafluoroethane					
Dichlorvos		0.869	11.6		0.00007 daphnia pulex **
Dicrotophos	6.3	2.6			
Dicumyl peroxide					
Dicyclopentadiene					
Dieldrin	0.01	0.008	0.016		0.250 daphnia pulex **
Diepoxybutane					
Diethanolamine			> 100	1.4	
Diethyl carbonate					
Diethyl chlorophosphate					
Diethyl methyl amine					
Diethyl phthalate		110 (S)			
Diethyl sulfate					
Diethyl-m-toluamide			110		
Diethyl-p-nitrophenyl phosphate					
Diethylamine	103.5		855	56.0 **	
Diethylarsine					
Diethylbenzene			4.15		
Diethylene glycol			> 100	0.3 - 1.0	
Diethylene glycol dimethyl ether					
Diethylene glycol monobutyl ether		1300		2850 *	2700 goldfish *
Diethylene glycol monobutyl ether acetate					
Diethylene glycol monoethyl ether		10000			
Diethylene glycol monoethyl ether acetate					
Diethylene glycol monomethyl ether		7500			
Diethylenetriamine					
Diethylhexyl phosphoric acid	48 - 54			17.2	
Diethylzinc					
Difluoroethane					
Difluorophosphoric acid					
Diisobutyl ketone					
Diisobutylcarbinol					
Diisobutylene					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr, unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Diisodecyl phthalate					
Diisopropanolamine					
Diisopropylamine	37				
Diisopropylbenzene hydroperoxide					
Dimefox					
Dimethoate	20 *	28 *			
Dimethyl (4-methylthio) phenyl phosphate					
Dimethyl acetamide	17				
Dimethyl carbamoyl chloride					
Dimethyl ether					
Dimethyl ethyl amine					
Dimethyl formamide	11000	7100			
Dimethyl hydrazine					10.1 guppy hard water
Dimethyl phosphorochloridothioate					
Dimethyl phthalate		50 (S)			
Dimethyl sulfate		7.5			
Dimethyl sulfide					
Dimethyl sulfoxide		TLm:33500 **			
Dimethyl terephthalate					
Dimethyl-p-phenylenediamine					
Dimethylamine	10.5				
Dimethyldichlorosilane					
Dimethylhexane dihydroperoxide					
Dimethylphenethylamine					
Dimethylzinc					
Dimetilan					
Dinitramine	0.58	1.52	1.44		
Dinitroaniline			14.85		
Dinitrobenzene			0.71	43.0 **	
Dinitrocresols				TLm:8 **	
Dinoseb			0.565	0.24 **	0.118 channel catfish
Dinoterb					
Dioctyl adipate					
Dioctyl phthalate					
Dioctyl sodium sulfosuccinate					
Dioxane		> 10000		4700.0 *	
Dioxathion		0.034	0.3		
Dioxolane					
Dipentene					
Diphacinone					
Diphenyl	log BCF:2.04				
Diphenyl ether	log BCF:2.20		4	0.07 **	
Diphenylamine					
Diphenyldichlorosilane					
Diphenylguanidine					
Diphenylmethane-4,4'-diisocyanate					
Dipropylamine					
Dipropylene glycol					
Dipropylnitrosamine					
Diquat	11.2 **	35	14		90.3 guppy [illegible]
Disodium arsenate					
Disodium hexafluorosilicate					
Disulfoton		0.063	3.7		
Dithiazanine iodide					
Dithiobiuret					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr, unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Dithiocarbamic acid					
Diuron	16	7.5	14.2	0.4	
Dodecene					
Dodecyl mercaptan					
Dodecylbenzene					
Dodecylbenzenesulfonic acid	3.2 - 5.6			10.07 **	
Dodecyltrichlorosilane					
Endosulfan	0.0003		TLm 0.00086	0.0520	
Endothall	0.77	1740	320		
Endothion					
Endrin	0.0006	0.0006	0.001		0.02 daphnia pulex **
Epichlorohydrin		35			23 goldfish *
EPN		0.1	110		
Eptam	19	27		6.7 **	
Ethane					
Ethanethioamide					
Ethanolamine	150	329.16	170 (S)	140.0 *	170 goldfish
Ethion	0.50	0.22			
Ethoxy triglycol					
Ethoxydihydropyran					
Ethoxyquin					
Ethyl 4,4'-dichlorobenzilate					
Ethyl acetate	484.86		230	710.0 **	202.5 daphnia pulex **
Ethyl acetoacetate					
Ethyl acrylate					
Ethyl alcohol	13000		14200	> 1000	12100 d.pulex (3/4 days)
Ethyl butanol					
Ethyl butyrate				755.0 *	
Ethyl chloride					
Ethyl chloroacetate					
Ethyl chloroformate					
Ethyl ether		> 10000			2130 guppy (14 days)
Ethyl formate					
Ethyl lactate					
Ethyl mercaptan					
Ethyl methacrylate					
Ethyl methanesulfonate					
Ethyl nitrite					
Ethyl phosphonothioic dichloride					
Ethyl propyl acrolein					
Ethyl silicate					
Ethyl thiocyanate					
Ethyl Toluene					
Ethylaluminum dichloride					
Ethylaluminum sesquichloride					
Ethylamine					
Ethylbenzene			12.1		
Ethylbis(2-chloroethyl) amine					
Ethyldichlorosilane					
Ethylene					
Ethylene chlorohydrin					
Ethylene cyanohydrin	35.0	21.5	90.7	100 **	
Ethylene diamine	230 (S) **		> 1000	29.5 **	
Ethylene dibromide		18 **			
Ethylene dichloride			550		

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr, unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Ethylene fluorohydrin					
Ethylene glycol					> 5000 goldfish *
Ethylene glycol diacetate		90		215 *	
Ethylene glycol diethyl ether					
Ethylene glycol dimethyl ether					
Ethylene glycol monobutyl ether		1490			1650 goldfish *
Ethylene glycol monobutyl ether acetate					
Ethylene glycol monoethyl ether		> 10000			
Ethylene glycol monoethyl ether acetate					
Ethylene glycol monomethyl ether	15520	> 10000			> 5000 goldfish *
Ethylene oxide				212.3 **	90 goldfish *
Ethylene thiourea	1800 (60 days)			26.4 **	
Ethylenediaminetetraacetic acid		159 (S)		625 *	
Ethyleneimine				14.0 *	
Ethylhexaldehyde					
Ethylhexanol	32 - 37		28.2		
Ethylhexoic acid					
Ethylhexyl acrylate					
Ethylidene norbornene					
Ethylmercuric phosphate					
Ethylphenyldichlorosilane					
Ethyltrichlorosilane					
Famphur					
Fenitrothion	2.4	2.8	2.4		0.0082 A.pulex (0.13 days)
Fensulfothion					
Ferric ammonium oxalate					
Ferric chloride				5.2 (100.8 hrs)	
Ferric fluoride					
Ferric hydroxide					
Ferric nitrate					
Ferric oxide					
Ferric sulfate					
Ferrous ammonium sulfate					
Ferrous chloride					
Ferrous oxalate					
Ferrous sulfate					
Flamprop-methyl					
Fluenetil					
Fluoboric acid					
Fluometuron		83			
Fluoranthene	CF:370 ***	4		320.0 **	
Fluorene					
Fluorine	TLm 2.3				
Fluoroacetamide				> 40 (0.13 days)	
Fluoroacetic acid					
Fluoroacetyl chloride					
Fluorouracil					
Fluosilicic acid					
Fluosulfonic acid					
Fonofos	0.110 *	0.045 *			
Formaldehyde	63.36	38.40		52.0 *	
Formaldehyde cyanohydrin					
Formic acid		175 *			
Formothion					
Fumaric acid					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr, unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Furan			01		
Furazolidone	> 30 (S)				
Furfural			32 (S)		
Furfuryl alcohol				115.0 *	
Gallic acid					
Glutamic acid					
Glutaraldehyde					
Glycerine	54000			> 10000 *	
Glycidyl methacrylate					
Glycidylaldehyde					
Glyoxal					
Glyphosate	8.3		2.3		
Heptachlor	0.019	0.019	0.056		0.042 daphnia pulex **
Heptachlorepoxide					
Heptane				10.0 *	4.0 goldfish *
Heptanol	43 **		34.6	70.2 **	49.0 daphnia pulex **
Heptene				> 50.0 *	
Herbadox					
Herban					
Herbisan					
Hexachloronaphthalene					
Hexachlorobenzene	< 0.030 **	12			
Hexachlorobutadiene	0.32	0.324	0.09		TLm 0.10 goldfish
Hexachlorocyclopentadiene		25	0.007		
Hexachloroethane	0.955	0.86	1.425	5.56 **	10.0 daphnia pulex **
Hexachlorophene			0.021		
Hexachloropropene					
Hexadecyltrimethylammonium bromide					
Hexaethyl tetraphosphate					
Hexaldehyde			22		
Hexamethylene diamine					
Hexamethylene tetramine			49000		
Hexamethyleneimine					
Hexamethylphosphoramide				6870.0 **	
Hexane				> 50.0 *	4.0 goldfish *
Hexanol			97.7		
Hexylene glycol		> 10000			
Hydrazine		1.162		0.01 *	3.85 guppy hard water
Hydrochloric acid		3.5			
Hydrocyanic acid	0.057 (F)	275 - 0.125	(1.7 - 0.161 (F)		
Hydrofluoric acid					
Hydrogen					
Hydrogen bromide					
Hydrogen chloride					
Hydrogen peroxide					
Hydrogen selenide					
Hydrogen sulfide	0.025	0.0258	TLm 0.0071 - 0.55		
Hydroquinone	0.097		0.14	0.05	
Hydroxyacetic acid					
Hydroxylamine sulfate			7.2	1.2	
Hydroxypropyl acrylate			3.505		
Hydroxypropyl methacrylate					
Indeno(1,2,3-cd)pyrene					
Iodine					
Iodomethane					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Iridium 192					
Isoamyl acetate					
Isoamyl alcohol					
Isobenzan					
Isobutane					
Isobutyl acetate				250.0 *	
Isobutyl acrylate			2.09		
Isobutyl alcohol					
Isobutylamine					
Isobutylene					
Isobutyraldehyde					
Isobutyric acid					
Isobutyronitrile					
Isodecaldehyde					
Isodecyl acrylate					
Isodecyl alcohol					
Isodrin		0.012 *			
Isooctaldehyde					
Isooctyl alcohol				100 *	
Isopentane					
Isophorone		220	145	120.0 **	
Isophorone diisocyanate					
Isophthalic acid					
Isoprene		42.54	TLm: 87 - 74 (24-96hrs)		
Isopropanolamine			> 5000 *		
Isopropyl acetate				1250.0 *	
Isopropyl alcohol			11130		
Isopropyl chloroformate					
Isopropyl ether		7000	786		380 goldfish *
Isopropyl formate					
Isopropyl mercaptan					
Isopropyl percarbonate					
Isopropylamine					
Isopropylmethylpyrazolyl dimethylcarbamate					
Isovaleraldehyde			3.25		
Kelthane					0.78 - 2.14 grass shrimp **
Kepone	0.036	0.051			
Lactic acid					
Lactonitrile		0.9	TLm: 0.9		TLm: 1.37 guppy
Lauric acid					
Lauroyl peroxide					
Lauryl alcohol					
Lauryl mercaptan					
Lead acetate		250			
Lead arsenate		TLm:1.4 **			
Lead chloride	0.180 **** *	232.9			
Lead chromate					
Lead dioxide					
Lead fluoride					
Lead fluoroborate			18		
Lead iodide					
Lead nitrate	8	6.3 **		0.15 **	
Lead oxide					
Lead phosphate					
Lead stearate					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Lead sulfate					
Lead sulfide					
Lead tetraacetate					
Lead thiocyanate					
Lewisite					
Lignin sulfonate	7300 (S) **				
Lithium	9.28 *** *				
Lithium aluminum hydride					
Lithium bromide					
Lithium carbonate					
Lithium chromate					
Lithium hydride					
Magnesium					
Magnesium chloride				888.4 (100.8hrs)	
Magnesium hydroxide					
Magnesium perchlorate					
Magnesium sulfate		3800 *		459.3	
Malathion	0.17	0.11	9	0.0018 **	0.0018 daphnia pulex **
Maleic acid			TLm: 5		
Maleic anhydride		138.0 **			
Maleic hydrazide					125 harlequin fish (F)
Malononitrile	1.63	0.57	0.56		
Maneb	2.56			1.0 **	
Mannitol					
MCPA		100 **			147 brown trout (S) *
MCPB					
Melamine					
Mephosfolan					
Mercaptobenzothiazole					
Mercaptodimethur					
Mercuric acetate			0.19		
Mercuric ammonium chloride					
Mercuric chloride	0.2775	0.118		0.025 **	0.022 daphnia pulex **
Mercuric cyanide				TLm:0.02 **	
Mercuric iodide					
Mercuric nitrate					
Mercuric oxide					
Mercuric sulfate					
Mercuric sulfide					
Mercuric thiocyanate			0.15		
Mercurous chloride					
Mercurous nitrate	0.033		0.168		
Mercury	0.005 *** *				
Mercury fulminate					
Mesityl oxide					540 goldfish *
Mesitylene					TLm: 13 goldfish
Methacrylamide					
Methacrylic anhydride					
Methacrylonitrile					
Methacryloyl chloride					
Methallyl chloride					14 goldfish *
Methane					
Methanesulfonyl fluoride					
Methidathion					
Methiocarb	0.8	0.16			

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Methoxychlor	0.0447	0.052	0.0075	0.006	0.00078 daphnia pulex **
Methoxyethylmercuric acetate					
Methyl 2-chloroacrylate					
Methyl acetate			368.5		
Methyl acrylate					
Methyl alcohol	19550	15450	29000	> 100	
Methyl amyl acetate					
Methyl amyl alcohol					360 goldfish *
Methyl bromide		11			
Methyl butyl ether					
Methyl butyl ketone					
Methyl chloride		550			
Methyl chloroformate					
Methyl disulfide					
Methyl ethyl ketone					5000 goldfish *
Methyl ethyl ketone peroxide					
Methyl ethyl phenol methyl carbamate					
Methyl ethyl pyridine					
Methyl hexyl ketone					
Methyl hydrazine					3.26 guppy hard water
Methyl isobutyl ketone					460 goldfish *
Methyl isocyanate					
Methyl isopropenyl ketone					
Methyl isothiocyanate					
Methyl mercaptan					
Methyl methacrylate		232.2	150	1760 *	TLm: 368 guppy
Methyl parathion	2.75	5.72	8.9		8.2 guppy
Methyl phenkapton					
Methyl salicylate					
Methyl thiocyanate					
Methyl trichlorosilane					
Methyl vinyl ketone					
Methylacetylene					
Methylamine					
Methylaniline					
Methylcyclopentadienyl manganese tricarbonyl					
Methylcyclopentane					
Methyldichlorosilane					
Methylene chloride	13.94 (d 7)	220	330	220 **	
Methylethanolamine					
Methylformate					
Methylmercuric dicyanamide					
Methylpyrrolidone					
Methylstyrene			10		
Methylthiouracil					
Methyltrichlorosilane					
Methyomyl					
Metobromuron	36	40			
Metolcarb					
Mevinphos	0.034 *	0.07			0.00016 daphnia pulex
Mexacarbate	11.1	22.8	23.7		22.3 atlantic salmon
Molybdenum trioxide					
Monocrotophos					450 harlequin fish (F)
Morpholine	280	350		100 *	
MTBA					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
N,N'-Dibutyl phthalate					
N,N'-Diethylhydrazine					
N,N-Diethyl-p-phenylenediamine					
N,N-Dimethylaniline			65.4		
N-(4-Ethoxyphenyl) acetamide					
N-(Aminothioxomethyl) acetamide					
N-9H-Fluorenyl acetamide					
N-Butyl-N-nitroso-1-butanamine					
N-Ethyl-N-nitroso carbamide					
N-Ethyl-N-nitroso ethanamine					
N-Nitrosodiphenylamine		5.8		7.8 **	
N-Nitrosomorpholine					
N-Nitrosopiperidine					
N-Nitrosopyrrolidine					
Nabam					
Naled	0.132	0.18			0.0011 daphnia pulex
Naphtha (HAN)		2.1 - 4.2	4.2 - 20.8	0.42 - 2.3 **	
Naphthalene	1.6		6.14	4.6 **	1.0 daphnia pulex
Naphthol	0.070 ** *		4.63	3.54 **	
Neohexane					
Neopentyl glycol					
Nickel acetate					
Nickel ammonium sulfate					
Nickel bromide					
Nickel carbonyl					
Nickel chloride	8.93	5.27		1.5	
Nickel cyanide					
Nickel fluoborate					
Nickel formate					
Nickel hydroxide					
Nickel nitrate	35.5			0.915 **	
Nickel sulfate	33.97 **	188 *			
Nicotine sulfate	7.31	4.31	12.2		
Nitralin	30	62			
Nitric acid					
Nitric oxide					
Nitrilotriacetic acid	98	198	> 100	950 *	
Nitroanaline				24 *	
Nitrobenzene	.002 (days ?	43	119	27 **	
Nitroethane					
Nitrofen					
Nitrogen (liquefied)					
Nitrogen dioxide					
Nitrogen tetroxide					
Nitroglycerin	2.8	1.856		32 **	
Nitromethane			> 650		
Nitrophenol	7.9	8.3	45.8	32.7	
Nitropropane			> 612		
Nitrosodimethylamine	770 (10 days)				
Nitrosoguanidine					
Nitrosyl chloride					
Nitrotoluene			25.6		
Nitrous oxide					
Nonane					
Nonanoic acid			104		

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Nonanol			5.7		
Nonene					3.0 goldfish *
Nonylphenol			0.14		
Norbormide					
Octachloronaphthalene		> 600		> 530 **	
Octamethyl pyrophosphoramide		120			
Octane			14.05	.3 mmol/m3 **	
Octanol				47 *	
Octene					
Octyl aldehyde					
Oleic acid			205		
Oleum		24 *			
Oxalic acid					
Oxydisulfoton					
Oxygen (liquefied)					
p-Cresidine					
p-Phenylenediamine					
Paraldehyde					
Paraquat	15				3.7 daphnia pulex **
Paraquat dimethylsulfate					
Parathion		0.065	1.41	0.00037 **	0.0008 daphnia pulex **
PCBs	.054 (5 days)			0.1 **	
Pentaborane					
Pentachlorobenzene	0.250 (6 d)	0.25		5.3 **	
Pentachloroethane		7.2	7.53	7.66 **	
Pentachloronitrobenzene					
Pentachlorophenol	0.938	0.167	0.274	0.53	1.1 daphnia pulex **
Pentadecanol					
Pentadecylamine					
Pentaerythritol					
Pentane					
Pentene					
Peracetic acid					
Perchloric acid					
Perchloromethyl mercaptan					
Phenanthrene	0.035 (1.06 days)			0.772 **	0.1 daphnia pulex
Phenol	0.15	18.52	36.97	4	76.87 daphnia pulex **
Phenyl hydrazine hydrochloride					
Phenyl mercuric acetate					
Phenyldichloroarsine					
Phenylsilatrane					
Phenylthiourea					
Phorate					0.0006 scud
Phosacetim					
Phosfolan					
Phosgene					
Phosmet	0.388	0.768	7.3	0.76 **	11 channel catfish
Phosphamidon	6	3.4	100	0.004 (1.08d	8.8 daphnia pulex **
Phosphine					
Phosphoric acid					
Phosphorus oxychloride					
Phosphorus pentasulfide					
Phosphorus pentoxide					
Phosphorus red		TLm:0.105 **			
Phosphorus tribromide					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Phosphorus trichloride					
Phosphorus white		TLm:0.105 **			
Phthalic acid					
Phthalic anhydride					
Picloram	11.6				TLm: 1.66 - 4.96 lake trout
Picric acid					
Piperazine					
Piperidine					
Polyaromatic hydrocarbons					
Polyphosphoric acid					
Potassium					
Potassium aluminate					
Potassium arsenate					
Potassium arsenite					
Potassium binoxalate					
Potassium bromate					
Potassium carbonate					
Potassium chlorate				589.0 *	
Potassium chloride		1006.5		14.5	
Potassium chromate			45.6 (S)	0.18	0.238 daphnia pulex **
Potassium cyanide	0.0578	0.18			
Potassium dichloroisocyanurate					
Potassium dichromate		TLm:738 *			
Potassium fluoride					
Potassium hydroxide					
Potassium iodide	896			7.5	
Potassium metabisulfite					
Potassium nitrate		810		10.2	
Potassium oxalate					
Potassium permanganate	0.506	0.827			
Potassium peroxide					
Potassium silver cyanide					
Potassium sorbate					
Potassium sulfate		653			
Promecarb					
Propane					
Propanolamine					
Propargite					
Propargyl alcohol			1.53		
Propargyl bromide					
Propiolactone					
Propionaldehyde		130			
Propionic acid		188 *		50 **	
Propionic anhydride		TLm:188 *			
Propionitrile					
Propoxur					
Propyl acetate			60	511 *	
Propyl alcohol	3200 **	> 1400	7140	7415	302.5 daphnia pulex **
Propyl chloroformate					
Propyl mercaptan					
Propylamine			306		
Propylene					
Propylene chlorohydrin					
Propylene glycol (poly)	>10000	> 1700			
Propylene glycol methyl ether					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Propylene glycol, allyl ether					
Propylene oxide		141			TLm: 141 mosquito fish
Propyleneimine					
Prothoate					
Pseudocumene			7.72		
Pyrene					TLm:0.0026 mosquito fish (S)
Pyridine	4.6		99.9	1320.7 **	575 daphnia pulex **
Pyrocatechol	8.9				
Pyrogallic acid					
Quinoline	0.8 (23 days)		TLm: 46	34.5 **	
Quinone			53.4		
Resorcinol	> 100		53 (S)		42 grass shrimp
Rotenone	0.046	0.109	0.004		0.0275 daphnia pulex *
Salicylic acid			1765		
Sarin					
Selenium dioxide		28.5	TLm: 7.3		
Selenium disulfide					
Selenium oxychloride					
Selenium trioxide					
Selenourea					
Selenous acid					
Semicarbazide hydrochloride					
Silicon tetrachloride					
Silver acetate					
Silver carbonate					
Silver cyanide					
Silver fluoride					
Silver iodate					
Silver nitrate	0.0557	0.0365			
Silver oxide					
Silver sulfate					
Sodium					
Sodium acetate		5000 *		7170 *	
Sodium aluminate					
Sodium amide					
Sodium anthraquinone sulfate					
Sodium arsenate	10.8 (F)				
Sodium arsenite	23				
Sodium azide	0.8	0.7			
Sodium benzoate					
Sodium bicarbonate		8600			
Sodium bifluoride					
Sodium bisulfate					
Sodium bisulfite				27	
Sodium borate	1800 (S) **				
Sodium borohydride					
Sodium bromide				10100 **	
Sodium cacodylate					
Sodium carbonate		160		262	
Sodium chlorate	2750 **				
Sodium chloride		1294.6	7650 (S)	3114 (100.8	
Sodium chlorite					
Sodium chromate	26.664				
Sodium cyanide	0.0817	0.149		0.09	
Sodium dichloroisocyanurate					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Sodium dichromate	68	410 **		4 **	
Sodium ferrocyanide				540	
Sodium fluoaluminate					
Sodium fluoride	106.3			109 - 354	
Sodium fluoroacetate					
Sodium fluorosilicate		49			
Sodium formate		5000			
Sodium hydride					
Sodium hydrosulfite					
Sodium hydroxide		9.9			
Sodium hypochlorite					
Sodium metabisulfite					
Sodium methanearsonate		71000 **			
Sodium methylate					
Sodium nitrate	1587.75	2600		2040.85 ***	
Sodium nitrilotriacetic acid	98.0 (days ?)				
Sodium nitrite					
Sodium oxalate		4000 *			
Sodium pentachlorophenate					
Sodium perchlorate					
Sodium phosphate, dibasic					
Sodium phosphate, monobasic				126 (100.8hrs)	
Sodium phosphate, tribasic					
Sodium phosphide					
Sodium selenite					
Sodium silicate				49.6	
Sodium sulfate		3040		709.25	
Sodium sulfide		25 **		8.0 (100.8hrs)	
Sodium sulfite				52.0 (100.8hrs)	
Sodium thiocyanate					
Sodium thioglycolate					
Sodium thiosulfate				805.0 (100.hrs)	
Sodium tripolyphosphate					
Sorbic acid					
Sorbitol					
Stannic chloride					
Stannous chloride	0.4 *** *			19.5 **	
Strontium	5.17 *** *				
Strontium chromate					
Strontium nitrate					
Strontium sulfide					
Strychnine		0.87			
Strychnine sulfate					
Styrene	2.5 **	25.05	29	41 **	
Styrene oxide					
Sulfamic acid			70.3 (S)		
Sulfolane					
Sulfotepp		0.0016			
Sulfur		10000 **			
Sulfur chloride					
Sulfur dioxide					
Sulfur tetrafluoride					
Sulfur trioxide					
Sulfuric acid		42 ** (S)			
Sulfuryl chloride					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Sulfuryl fluoride					
Tabun					
Tall oil					
Tannic acid					
Tartaric acid					
TCDD					BCF: 4875 mosquito fish (7 days
Tebuthiuran					
Tellurium hexafluoride					
Temephos	0.158				
Terephthalic acid					
Terphenyl					
tert-Butyl acetate					
Tetrabutyl titanate					
Tetrachloroethane		20	20.3	43.8 **	48.48 daphnia pulex **
Tetrachloroethylene	5.415	13	16.65	13.57 **	
Tetrachlorvinphos					
Tetradecanol			19.45		
Tetradecene					
Tetradecylbenzene					
Tetraethyl lead		0.02			
Tetraethyl pyrophosphate	0.7	0.977	1.9		
Tetraethylene glycol					
Tetraethylene pentamine					
Tetraethyltin					
Tetrafluoroethylene					
Tetrahydrofuran			2160	> 10000 *	
Tetrahydronaphthalene					
Tetramethyl lead		84			
Tetranitromethane					
Tetrasodium pyrophosphate					
Thallic peroxide					
Thallium	0.180 *** *				
Thallium acetate		170			
Thallium carbonate					
Thallium chloride					
Thallium nitrate				1.142 *	
Thallium sulfate	1.5 (10 days	> 800		2.2 **	
Thioglycolic acid			30		
Thiometon					3.2 harlequin fish
Thionazin					
Thionyl chloride					
Thiophan sulfone					
Thiophenol					
Thiophosgene					
Thiosemicarbazide					
Thiourea			> 100	1.8	
Thiram					
Thorium dioxide					
Thorium nitrate				1000 **	
Titanium dioxide					
Titanium tetrachloride					
Toluene	0.02	TLm: 24.0	36.2		22.8 goldfish
Toluene-2,4-diamine		(24-96hrs)	BCF: 91 (32 days)		
Toluene-2,4-diisocyanate			165.5 (S)		
Toluenesulfonic acid					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Toluidine			149		
Tolyl thiourea					
Toxaphene	0.011	0.0036	0048 (10day	0.015 **	0.015 daphnia pulex **
Tri(2-butoxyethyl) phosphate					
Tri-o-cresyl phosphate		7000			
Triallate					
Triamiphos					
Tributyl phosphate	5 - 9 (S)		9.59		
Trichlorofon	4.95(S)	3.8	109		0.00018 daphnia pulex **
Trichloro triazine					
Trichloroacetaldehyde					
Trichloroacetyl chloride					
Trichlorobenzene	2.806	3.21		1.68 **	
Trichlorocyanuric acid					
Trichloroethane		40	58.93	40 ***	
Trichloroethyl amine					
Trichloroethylene	42 **	45	44.1	58.1 **	45 daphnia pulex **
Trichlorofluoromethane					
Trichloronate					
Trichlorophenol	0.73	0.0004	6.865	3.36	
Trichlorophenoxy propionic acid	0.64	83 **			
Trichlorophenyl silane					
Trichlorosilane					
Trichlorotrifluoroethane					
Tridecene					
Tridecyl alcohol			0.64		
Triethanolamine				1390 *	> 5000 goldfish *
Triethoxysilane					
Triethylaluminum					
Triethylamine		> 100			
Triethylbenzene					
Triethylene glycol		> 10000	69800		62000 guppy (7 days)
Triethylene tetramine					
Trifluorochloroethylene					
Trifluralin	0.13	0.119	TLm: 0.115	0.193 **	0.240 daphnia pulex **
Triisobutylaluminum					
Trimellitic anhydride					
Trimethylamine					
Trimethylchlorosilane					
Trimethylene bromide					
Trimethylene chloride					
Trinitrobenzene					
Trinitrotoluene	1.2	2.62	2.58 (F)	9.25	
Triphenyltin chloride					
Tripropylene glycol					
Tris(1-aziridinyl) phosphine oxide					
Trisodium nitrilotriacetate					
Turpentine					
Undecanol					
Undecylbenzene					
Uranium dioxide					
Uranium hexafluoride					
Uranyl acetate			TLm: 3.7		
Uranyl nitrate			TLm: 3.1		
Uranyl sulfate					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
Urea				> 10000 *	
Urea peroxide					
Urethan					
Valeraldehyde			12.9		
Vanadium oxide					
Vanadium oxytrichloride					
Vanadium pentoxide	11.7				
Vanadyl sulfate					
Vinyl acetate		18	22	330 *	
Vinyl bromide					
Vinyl chloride					
Vinyl fluoride					
Vinyl methyl ether					
Vinyl styrene					
Vinylidene chloride		220			
Vinylnorbornene					
Vinyltrichlorosilane					
Warfarin					12.0 harlequin fish (S)
Xylene	13	17.79	16.6	0.233	
Xylenol	3.2 - 5.6 (S)		14 (S)		
Zinc acetate	0.55		TLm: 0.88		
Zinc ammonium chloride					
Zinc arsenate					
Zinc borate					
Zinc bromide					
Zinc carbonate					
Zinc chloride	4	2.86 - 4.2		0.0679	
Zinc chromate					
Zinc cyanide					
Zinc fluoborate					
Zinc fluoride					
Zinc formate					
Zinc hydrosulfite					
Zinc nitrate					
Zinc oxide					
Zinc phenolsulfonate					
Zinc phosphate	0.09				
Zinc phosphide					
Zinc silicofluoride					
Zinc stearate		chemical too insoluble to be toxic			
Zinc sulfate	2.06	3.3	TLm: 14		
Zirconium acetate					
Zirconium nitrate					
Zirconium oxychloride					
Zirconium potassium fluoride					
Zirconium sulfate					
Zirconium tetrachloride					
(2-Chlorophenyl) thiourea					
1,1-Dichloropropane		98		23 **	
1,2,4,5-Tetrachlorobenzene	10	1.6		530 **	
1,2-Benzisothiazolin-3-one 1,1-dioxide					
1,2-Dibromo-3-chloropropane					
1,2-Dihydro-3-methyl benz(j)aceanthrylene					
1,2-Diphenylhydrazine		0.23 - 0.27		4.1 **	
1,2-Ethanediylbiscarbamodithioic acid					

Aquatic Toxicity	Lethal Toxicity to Species (LC50-96hr. unless noted)				
Chemical	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Other
1,2-Methylenedioxy-4-allyl benzene					
1,2-Methylenedioxy-4-propenyl benzene					
1,2-Methylenedioxy-4-propyl benzene					
1,2-Oxathiolane-2,2-dioxide					
1,2:7,8-Dibenzopyrene					
1,4-Dichloro-2-butene					<< 40 guppy (7 days)
1,4-Naphthalenedione					
1-(Chloromethyl)-4-nitrobenzene					
1-Amino-2-methyl anthraquinone					
1-Bromo-4-phenoxy benzene					
1-Naphthylamine					
10,10'-Oxydiphenoxarsine					
2,2'-Thiobis(4,6-dichlorophenol)					
2,2'-Thiobis(4-chloro-6-methyl) phenol					
2,3,4,6-Tetrachlorophenol		0.14		0.29 **	
2,3-Dibromo-1-propanol phosphate	0.845				
2,3-Dichloropropene					
2,4,5-T	0.96 (R)		7100		26.1 guppy (S)
2,4,6-Trimethyl aniline					
2,4-dichlorophenoxyacetic acid (2,	358	203		90 - 220 **	70.7 guppy
2,4-Dinitrotoluene			33 - 48	35 **	
2,4-Dinitrophenol	1.16	2.295	11.38	4.7 **	
2,4-Dichlorophenol	2.6	2	7.75	2.6 **	
2,6-Dinitrophenol				0.075 (7 days)	
2,6-Xylidine					
2-Aminoanthraquinone					
2-Methyl benzenamine hydrochloride					
2-Methyl-5-vinyl pyridine					
2-Naphthylamine					
2-Phenylphenol			6.15		
2-Picoline			897		
3,3'-Dichloro(1,1'-biphenyl)-4,4'-diamine					
3,3'-Dimethyl(1,1'-biphenyl)-4,4'-diamine					
3,4-Dichlorophenyl isocyanate					
3,4-Dinitrotoluene					
3-(Trifluoromethyl) benzenamine					
3-Chloropropionitrile					
3-[p-Di(chloroethyl)amino] phenyl-L-alanine					
4'-Amino propiophenone					
4,4'-Diaminodiphenyl ether					
4,4'-Methylene dianiline					
4,4'-Methylenebis(2-chloro) anilene					
4,4'-Thiodianiline					
4,5-Dichloro-2-trifluoromethyl benzimidazole					
4,6-Dinitro-o-cyclohexylphenol					
4-Aminoazobenzene					
4-Aminobiphenyl					
4-Aminobutyl diethoxymethyl silane					
4-Aminopyridine		4.488			
4-Chlorobenzenamine					
4-Chlorophenyl phenyl ether					
4-Nitrobiphenyl					
5-chloro-2-(2,4-dichlorophenoxy) phenol					
5-Nitro-o-anisidine					
5-[Bis(2-chloroethyl)amino] uracil					

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Acenaphthene							
Acenaphthylene							
Acetaldehyde	134 /30m	4000/4h		20200/30m *			661
Acetamide							7000
Acetic acid							3530
Acetic anhydride				1000/4h			1780
Acetoacetanilide							4650
Acetone	12000/4h	16000/4h					9750
Acetone cyanohydrin		63/4h					17
Acetone thiosemicarbazide							
Acetonitrile		8000/4h		7551/8h	570		2730
Acetophenone							815
Acetoxytriphenyl stannane							447
Acetyl bromide							
Acetyl chloride	2/1m						
Acetyl peroxide							
Acetylacetone	1000/4h						1000
Acetylene	500000/5m						590
Acridine							
Acrolein	153/10m	8/4h		129/30m *			46
Acrylamide							124
Acrylic acid		4000/4h					340
Acrylonitrile	453/1h *	40-80/6h					
Acryloyl chloride		25/4h					
Adipic acid							
Adiponitrile				380/4h *			155
Alachlor							1200
Aldicarb							0.65
Aldrin				13/5h *	14	C: 1.25	39
Allyl alcohol	1000/1h			165/4h			64
Allyl bromide			817 *	177/8h			
Allyl chloride	3000			314/30m *			700
Allyl chloroformate				2195/2h *			244
Allylamine	5/5m		135 *	76/8h			102
Allyltrichlorosilane				4.4 *			
Aluminum (fume or dust)							
Aluminum chloride							3311
Aluminum fluoride							
Aluminum hydroxide					C: 122000		
Aluminum nitrate							264
Aluminum oxide							
Aluminum phosphate							
Aluminum sulfate							
Aminocarb							30
Aminoethylethanolamine							50
Aminopterin					F: 0.12		
Amiton							3.3
Amitrole							1100
Ammonia	20	2000/4h					350
Ammonium acetate							

TABLE A6 MAMMALIAN TOXICITIES

Note: m: minutes h: hours d: days w: weeks

C: child M: male F: female

	INHALATION				ORAL		
Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Ammonium benzoate							825
Ammonium bicarbonate							
Ammonium bisulfate							
Ammonium carbamate							
Ammonium carbonate							
Ammonium chlorate							
Ammonium chloride							1650
Ammonium chromate							
Ammonium citrate							
Ammonium dichromate							
Ammonium fluoborate							
Ammonium fluoride							
Ammonium formate							
Ammonium hydrogen fluoride							60
Ammonium hydroxide	5000				43		350
Ammonium iodide							
Ammonium molybdate							333
Ammonium nitrate							4820
Ammonium oleate							
Ammonium oxalate							
Ammonium pentaborate							
Ammonium perchlorate							
Ammonium persulfate							
Ammonium phosphate dibasic							689
Ammonium phosphate hemibasic							1000
Ammonium phosphate monobasic							
Ammonium picrate							1000
Ammonium silicofluoride							
Ammonium stearate							
Ammonium sulfamate							2000
Ammonium sulfate					1500		3000
Ammonium sulfide							
Ammonium sulfite							
Ammonium tartrate							
Ammonium thiocyanate							
Ammonium thiosulfate							
Ammonium vanadate							160
Amyl acetate	924/30m *						6500
Amyl alcohol		3819/6h					2200
Amyl chloride							
Amyl mercaptan		2000/4h					
Amyl methyl ketone		4000/4h					1670
Amyl nitrate		3593					
Amyltrichlorosilane		2000/4h					2340
Aniline		250/4h					250
Anisidine							2000
Anisoyl chloride							
Anthracene							
Antimony pentachloride				58/2h *			1115
Antimony pentafluoride							

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Antimony potassium tartrate					2		115
Antimony tribromide							
Antimony trichloride	8 *						525
Antimony trifluoride							
Antimony trioxide							20000
Arsenic					7857		
Arsenic acid							8
Arsenic disulfide							
Arsenic pentoxide							8
Arsenic trichloride							
Arsenic trioxide					1.429		40
Arsenic trisulfide							
Arsine	25/30m	93/3h *					
Asbestos							
Atlox							
Atrazine				580/4h *			3080
Azinphos ethyl							17.5
Azinphos methyl				5/1h *			13 - 16.4
Barban							6000
Barium							
Barium carbonate					29 - 57		418
Barium chlorate							
Barium chloride					11.4		118
Barium cyanide							
Barium nitrate							355
Barium perchlorate							
Barium permanganate							
Barium peroxide							
Barium sulfate							
Batrachotoxin (BTX)							
Benazolin							3000
Benzaldehyde							1300
Benzamide							
Benzene	2000/5m			10000/7h	50		3306
Benzene hexachloride					14000		177
Benzenearsonic acid							50
Benzenephosphorus dichloride							
Benzenephosphorus thiodichloride							
Benzenesulfonyl chloride				32/1h			1960
Benzidine							309
Benzoic acid					500		1700
Benzonitrile				950/8h			720
Benzophenone							1200 - 7400
Benzotrichloride				19/2h			6000
Benzotrifluoride				11657/4h *			15000
Benzoyl chloride	2/1m			320/2h *			
Benzoyl peroxide							7710
Benzo[b]fluoranthene							
Benzo[ghi]perylene							
Benzo[j,k]fluorene							2000

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Benzo[k]fluoranthene							
Benzyl alcohol				1000/8h			1230
Benzyl bromide							
Benzyl chloride				150/2h			1231
Benzyl chloroformate							
Benzyl cyanide				88/2h *			270
Benzyl-n-butyl phthalate							2330
Benzylamine							
Benzyltrimethylammonium chloride							250
Benz[a]acridine							
Benz[a]anthracene							
Beryllium							
Beryllium chloride	801 *						86
Beryllium fluoride							98
Beryllium nitrate							
Beryllium oxide							
Beryllium sulfate							82
Bismuth oxychloride							22000
Bisphenol A				200			3250
Bisphenol A diglycidyl ether							11000
Boric acid		11/4h *			F: 200		2660
Boron tribromide							
Boron trichloride		20/7h					
Boron trifluoride				419/4h *			
Bromine	1000				14		
Bromine pentafluoride							
Bromine trifluoride							
Bromoacetone	572/10m						
Bromobenzene				3127 *			2699
Bromochlorodifluoromethane				32/15m			
Bromoform		4283/4h *					1147
Bromotrifluoromethane				67194 *			
Bromoxynil							190
Brucine							1
Butadiene	8000			126717/4h *			5480
Butane				271019/4h *			
Butenediol							
Butyl acetate				2000/4h			13100
Butyl acrylate				2730/4h			900
Butyl alcohol				8000/4h			790
Butyl formate							406
Butyl hydroperoxide							
Butyl isovalerate							
Butyl mercaptan				4020/4h			1500
Butyl methacrylate				4910/4h			22600
Butyl peroxy-2-ethylhexanoate							
Butyl peroxypivalate							4300
Butyl vinyl ether							10000
Butylamine							380
Butylated hydroxytoluene							890

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Butylene							6460
Butylphenol							2951
Butyltrichlorosilane							
Butyraldehyde				58042/30m *			5900
Butyric acid							2000
Cacodylic acid				M: > 6.9/2h			644
Cadmium	9/20m *			5.9/30m *			225
Cadmium acetate							
Cadmium bromide							
Cadmium chloride							88
Cadmium fluoroborate							250
Cadmium nitrate							300
Cadmium oxide				146/10m *			72
Cadmium stearate							
Cadmium sulfate							280
Calcium arsenate							20
Calcium carbide							
Calcium carbonate							6450
Calcium chlorate							4500
Calcium chloride							1000
Calcium chromate							327
Calcium cyanamide							
Calcium cyanide							39
Calcium fluoride							4250
Calcium formate							2650
Calcium hydroxide							7340
Calcium hypochlorite							850
Calcium nitrate							3900
Calcium oxide							
Calcium peroxide							
Calcium phosphate							
Calcium phosphide							
Calcium propionate							3920
Calcium resinate							
Calcium sulfate							
Camphene							
Camphor oil					29		3730
Cantharidin					0.428		
Caprolactam	100			64/2h *			1210
Caprylic acid							10080
Captan							9000
Carbachol chloride							40
Carbamidoselenic acid							
Carbaryl							230
Carbofuran				9 *			11
Carbon dioxide	90000/5m	65600/15m					
Carbon disulfide	4000/30m			7899/2h *	14		3188
Carbon monoxide	5000/5m			1807/4h			
Carbon oxyfluoride				360/1h			
Carbon tetrachloride	50000/5m			8000/4h	F: 43		93

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Carbonyl sulfide		1400/75m					
Carbophenothion							32.2
Carboxymethylcellulose							27000
Cesium 137							
Cetyl alcohol							6400
Chloramben							5620
Chlordane					29		200
Chlorine	500/5m			293/1h			
Chlorine dioxide		500/15m					
Chlorine trifluoride		400/30m					
Chlormequat					10		430
Chloro nitrophenol							100
Chloro nitrophenol, sodium salt							
Chloro phenyl phenol							
Chloro toluidine hydrochloride							
Chloro-dinitrophenol							
Chloro-m-cresol							1830
Chloro-o-nitrobenzene							288
Chloroacetaldehyde							75
Chloroacetic acid				46 *			580
Chloroacetophenone	25/20m *	65/15m *					127
Chloroacetyl chloride		1000/4h					120
Chlorobenzene				12000/30m			2290
Chlorobenzoyl peroxide							
Chlorobutyronitrile							
Chlorocyclopentylphenol							
Chlorodibromomethane							848
Chlorodifluoroethane				490654/4h *			
Chlorodifluoromethane		250000/4h		350000/15m			
Chloroethylvinyl ether		250/4h					250
Chloroform	5038/5m	8000/4h		9.6/4h *	140		908
Chlorohydrin		125/4h					55
Chloromercuri dinitrophenol							
Chloromercuriphenol							100
Chloromethyl methyl ether				55/7h			500
Chloropentafluoroethane							
Chlorophacinone							2.1
Chlorophenol, potassium salt							587
Chloropicrin	0.3 *						250
Chloroprene		2280/4h					900
Chlorosulfonic acid							
Chlorothalonil							10000
Chlorotoluidine							1500
Chlorotrifluoromethane							
Chloroxuron							3700
Chlorpropham							1200
Chlorpyrifos							male: 183
Choline chloride							3400
Chromic acetate							
Chromic acid							80

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Chromic sulfate							
Chromium							
Chromous chloride							1870
Chromyl chloride							
Cobalt							1500
Cobaltous acetate							708
Cobaltous bromide							406
Cobaltous chloride					C: 1500		80
Cobaltous formate							
Cobaltous hydroxide							
Cobaltous nitrate							691
Cobaltous sulfamate							
Cobaltous sulfate							768
Copper acetate							595
Copper acetoarsenite							22
Copper arsenite							
Copper bromide							
Copper chloride							140
Copper cyanide							
Copper hydroxide					200		
Copper iodide							
Copper naphthenate							
Copper nitrate							940
Copper oxalate							
Copper oxide							470
Copper sulfate					50		300
Copper sulfate, ammoniated							
Copper tartrate							
Coumafuryl							
Coumaphos				20 *			16
Coumatetralyl							16.5
Cresol							1454
Crimidine							1.25
Crotonaldehyde				1373/30m *			160 - 300
Cumene				8000/4h			1400
Cumene hydroperoxide				220/4h			382
Cupferron							
Cyanoacetic acid							1500
Cyanogen	92/10m			350/1h			
Cyanogen bromide	92/10m						
Cyanogen chloride							
Cyanogen iodide							
Cyanophos							565
Cyanuric acid							7700
Cyanuric fluoride				3.1/4h			
Cyclohexane							12705
Cyclohexanol							2060
Cyclohexanone				8000/4h			1535
Cyclohexanone peroxide							
Cyclohexenyl trichlorosilane							2830

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Cycloheximide							2
Cyclohexylamine				1819 *			156
Cyclopentane							
Cyclophosphamide							94
Cyclopropane							
Dalapon							970
DDD							113
DDE							880
DDT					500		87
Decaborane				46/4h			64
Decabromodiphenyl oxide							
Decahydronaphthalene		500/4h					4170
Decaldehyde							3730
Decene							
Decyl alcohol							4720
Decyl benzene							
Decyl octyl phthalate							45000
Demeton		0.7/4h *			0.24		1.7
Demeton-S-methyl		52/4h *					60
Di(p-chlorobenzoyl) peroxide							
Diacetone alcohol							4000
Diallate							395
Diamyl phthalate							
Diazinon				277/4h *			300 - 400
Diazomethane							
Dibenzofuran							
Dibenz[a,h]anthracene							
Dibromomethane				5534/2h *			108
Dibutyl ether		4000/4h					7400
Dibutyl ketone							
Dibutyl phthalate				0.7 *			8000
Dibutylamine		500/4h					189
Dicamba							1039
Dichlobenil							2710
Dichlone							160
Dichloro trichloromethyl benzhydrol							575
Dichlorobenzidine							7070
Dichlorobromomethane							916
Dichlorodifluoroethane							
Dichlorodifluoromethane				> 800000/30m			> 1000
Dichloroethane							1120
Dichloroethoxy methane							
Dichloroethyl amino uracil							7.5
Dichloroethyl ether				59/4h *			75
Dichloroethylene				1000/7h	286		670
Dichlorofluoromethane				49900/4h			
Dichloroisopropyl ether		700/5h					240
Dichloromethyl ether	100/3m			7/7h			210
Dichloromethyl ketone							
Dichlorotetrafluoroethane				72/30m			56 - 80

TABLE A8	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Dichlorvos				1.6/4h *			32
Dicrotophos				62/1h *			13
Dicumyl peroxide							4100
Dicyclopentadiene		500/4h					353
Dieldrin				2.7/4h *	M: 65		38.3
Diethanolamine							710
Diethyl carbonate							
Diethyl chlorophosphate							11
Diethyl phthalate				813 *			8600
Diethyl sulfate		250/4h					880
Diethyl-m-toluamide				748 *			1950
Diethyl-p-nitrophenyl phosphate							1.8
Diethylamine				4000/4h			540
Diethylarsine							
Diethylbenzene							
Diethylene glycol					1000		20700
Diethylene glycol dimethyl ether							12565
Diethylene glycol monobutyl ether							6560
Diethylene glycol monobutyl ether acetate							6500
Diethylene glycol monoethyl ether							11000
Diethylene glycol monoethyl ether acetate							9210
Diethylene glycol monomethyl ether							1080
Diethylenetriamine							4940
Diethylhexyl phosphoric acid							
Diethylmethylamine							
Diethylzinc							
Difluoroethane		500000/30m					
Difluorophosphoric acid							
Diisobutyl carbinol							3560
Diisobutyl ketone		2000/4h					5750
Diisobutylene							
Diisodecyl phthalate							
Diisopropanolamine							6720
Diisopropylamine				1141/2h *			770
Diisopropylbenzene hydroperoxide							
Dimefox							1
Dimethoate						30	152
Dimethyl (4-methylthio) phenyl phosphate							
Dimethyl carbamoyl chloride				180/6h			1000
Dimethyl ether				160778 *			
Dimethyl phosphorochloridothioate				51/4h *			
Dimethyl phthalate							6800
Dimethyl sulfate	97/10m			8.6/4h *			205
Dimethyl sulfide				40240			535
Dimethyl sulfoxide							14500
Dimethyl terephthalate							4390
Dimethyl-p-phenylenediamine							
Dimethylacetamide				2475/1h			4830
Dimethylamine				4540/6h			698
Dimethyldichlorosilane		930/4h					

TABLE A8	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Dimethylethylamine							78
Dimethylformamide							2800
Dimethylhexane dihydroperoxide							
Dimethylhydrazine				252/4h			122
Dimethylphenethylamine					50		1410
Dimethylzinc							
Dimetilan							25
Dinitramine							3700
Dinitroaniline							418
Dinitrobenzene					28		83
Dinitrocresole							10
Dinoseb							25
Dinoterb							62
Dioctyl adipate							9110
Dioctyl phthalate							30600
Dioctyl sodium sulfosuccinate							1900
Dioxathion							20
Dioxolane		32000/4h		6704/4h *			3000
Dipentene							5000
Diphacinone							1.5
Diphenyl							2400
Diphenyl ether							3370
Diphenylamine							
Diphenyldichorosilane							
Diphenylguanidine							507
Diphenylmethane-4,4'-diisocyanate							5600
Dipropylamine				1046/4h *			460
Dipropylene glycol							14850
Dipropylnitrosamine							480
Diquat							120
Disodium arsenate							
Disodium hexafluorosilicate							125
Disulfoton							2.6 - 12.5
Dithiazanine iodide							
Dithiobiuret							5
Dithiocarbamic acid							
Diuron							1017
DL-Diepoxybutane				56/4h			210
Dodecene							
Dodecyl mercaptan							309
Dodecylbenzene							
Dodecylbenzenesulfonic acid							438
Dodecyltrichlorosilane							
Endosulfan				4.7/4h *			18
Endothall							51
Endothion							23
Endrin					171		3
Epichlorohydrin				360/6h			90
EPN							7
Eptam		25/4h *					1642

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Ethane							
Ethanethioamide							301
Ethanolamine							2050
Ethion							13
Ethoxydihydropyran							6160
Ethoxyquin							800
Ethoxytriglycol							11000
Ethyl 4,4'-dichlorobenzilate							700
Ethyl acetate				1600/8h			5620
Ethyl acetoacetate							3980
Ethyl acrylate		1000/4h		2180/4h			800
Ethyl alcohol				20000/10h	C: 2000		7060
Ethyl aluminum dichloride							
Ethyl benzene		4000/4h					3500
Ethyl butanol							1850
Ethyl butyrate							13000
Ethyl chloride				5985/2h *			
Ethyl chloroacetate							
Ethyl chloroformate				145/1h			270
Ethyl ether				73000/2h	420		1215
Ethyl formate		8000/4h					1850
Ethyl lactate							
Ethyl mercaptan				4420/4h			1960
Ethyl methacrylate		31611/3h *		8300/4h			14800
Ethyl methanesulfonate							
Ethyl nitrite							
Ethyl phosphonothioic dichloride		32/4h					900
Ethyl propyl acrolein							3000
Ethyl silicate		1000/4h					6270
Ethyl thiocyanate							
Ethyl trichlorosilane		500/4h					1330
Ethylaluminum sesquichloride							
Ethylamine		3000/4h					400
Ethylbis(2-chloroethyl) amine							
Ethyldichlorosilane							
Ethylene							
Ethylene chlorohydrin	M: 305/2	7/1h		87 *			71
Ethylene cyanohydrin							3200
Ethylene dibromide		400/2h			F: 90		108
Ethylene dichloride		1000/4h		3476/30m	286		670
Ethylene fluorohydrin				1000/7h			
Ethylene glycol					398 - 786		4700
Ethylene glycol diacetate							6850
Ethylene glycol diethyl ether		8000/4h					4390
Ethylene glycol dimethyl ether							
Ethylene glycol monobutyl ether				450/4h			470
Ethylene glycol monobutyl ether acetate							2400
Ethylene glycol monoethyl ether		4000/4h		2000/7h			3000
Ethylene glycol monoethyl ether acetate		1500/8h					2900
Ethylene glycol monomethyl ether		2000/4h		1500/7h	3380		2460

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Ethylene oxide				1460/4h			72
Ethylene thiourea							545
Ethylenediamine		4000/4h					1160
Ethylenediaminetetraacetic acid							4000
Ethyleneimine				58/2h *			15
Ethylhexaldehyde		4000/4h					3700
Ethylhexanol							2049
Ethylhexoic acid							3000
Ethylhexyl acrylate							5660
Ethylidene norbornene				1246-4000/4h			2527
Ethylmercuric phosphate					8.805		
Ethylphenyldichlorosilane							
Ethyltoluene							
Famphur							35
Fenitrothion				33/4h *			250
Fensulfothion							2
Ferric ammonium oxalate							
Ferric chloride							1872
Ferric fluoride							
Ferric hydroxide							
Ferric nitrate							3250
Ferric oxide							
Ferric sulfate							
Ferrous ammonium sulfate							3250
Ferrous chloride							984
Ferrous oxalate							
Ferrous sulfate					F: 200		319
Flamprop-methyl							5000
Fluenetil							6
Fluoboric acid							
Fluometuron							8900
Fluoranthene							2000
Fluorene				185/1h			
Fluorine					71 - 75		52
Fluoroacetamide							5.75
Fluoroacetic acid							4.68
Fluoroacetyl chloride							
Fluorouracil							230
Fluosilicic acid							
Fluosulfonic acid							
Fonofos							3
Formaldehyde				830/30m	F: 36		800
Formaldehyde cyanohydrin							16
Formic acid				7839/15m *			1100
Formothion							250
Fumaric acid							10700
Furan							
Furazolidone							2336
Furfural		153/4h					65
Furfuryl alcohol				233/4h			275

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Gallic acid							
Glutamic acid							
Glutaraldehyde		5000/4h					239
Glycerine							12600
Glycidyl methacrylate							597
Glycidylaldehyde		251/4h					
Glyoxal							2020
Glyphosate							470
Heptachlor							40
Heptachlorepoxide							47
Heptane							
Heptanol							3250
Heptene							
Herbadox							1250
Herban							2000
Herbisan							480
Hexachlorobenzene				287 *			10000
Hexachlorobutadiene							90
Hexachlorocyclopentadiene				1.6/4h			113
Hexachloroethane							4460
Hexachloronaphthalene							
Hexachlorophene				20 *	C: 250		56
Hexachloropropene				425/30m			
Hexadecyltrimethylammonium bromide							410
Hexaethyl tetraphosphate							7
Hexaldehyde		2000/4h					4890
Hexamethylene diamine							750
Hexamethylene imine		4800/4h					410
Hexamethylene tetramine							
Hexamethylphosphoramide							2525
Hexane	5000/10m						28710
Hexanol							720
Hexylene glycol							3700
Hydrazine				570/4h			60
Hydrochloric acid	1300/30m			3124/1h			
Hydrocyanic acid	107/1h *			484/5m	2.857		5
Hydrofluoric acid	50/30m			1276/1h			
Hydrogen							
Hydrogen bromide				2858/1h			
Hydrogen chloride	3000/5m			4701/30m *			
Hydrogen peroxide				1414/4h *	1429		
Hydrogen selenide							
Hydrogen sulfide	600/30m			444			
Hydroquinone					29		320
Hydroxyacetic acid							1950
Hydroxylamine sulfate							
Hydroxypropyl acrylate							250
Hydroxypropyl methacrylate							
Indeno(1,2,3-cd)pyrene							
Iodine		76/1h *					14

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Iodomethane		3790/15m		220/4h *			0.15 - 0.22
Iridium 192							
Isoamyl acetate							16600
Isoamyl alcohol							1300
Isobenzan							4.8
Isobutane				570000/15m			
Isobutyl acetate		8000/4h					13400
Isobutyl acrylate		2000/4h					7460
Isobutyl alcohol		8000/4h					2460
Isobutylamine							228
Isobutylene				265743/4h *			
Isobutyraldehyde		8000/4h					2810
Isobutyric acid							280
Isobutyronitrile		1000/4h					50
Isodecaldehyde							
Isodecyl acrylate							12000
Isodecyl alcohol							6400
Isodrin							7
Isooctaldehyde							
Isooctyl alcohol							1480
Isopentane							
Isophorone		1840/4h					2330
Isophorone diisocyanate				13/4h *			
Isophthalic acid							10400
Isoprene				63551/4h *			
Isopropanolamine							2098
Isopropyl acetate		32000/4h		11915/8h *			3000
Isopropyl alcohol				16000/8h			5045
Isopropyl chloroformate		200/5h					1070
Isopropyl ether				38129 *			8470
Isopropyl formate							
Isopropyl mercaptan							1710
Isopropyl percarbonate							2140
Isopropylamine		8000/4h		4000/4h			820
Isopropylmethylpyrazolyl dimethylcarbamate							11
Isovaleraldehyde		16000/4h					8910
Kelthane							575
Kepone							95
Lactic acid							3730
Lactonitrile		125/4h					87
Lauric acid							12000
Lauroyl peroxide							
Lauryl alcohol							12800
Lauryl mercaptan							
Lead acetate							
Lead arsenate							100
Lead chloride							
Lead chromate							
Lead dioxide							
Lead fluoride							

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Lead fluoroborate							50
Lead iodide							
Lead nitrate							
Lead oxide							
Lead phosphate							
Lead stearate							
Lead sulfate							
Lead sulfide							
Lead tetraacetate							
Lead thiocyanate							
Lewisite	6/30m						
Lignin sulfonate							
Lithium							
Lithium aluminum hydride							
Lithium bromide							
Lithium carbonate							525
Lithium chromate							
Lithium hydride		67/4h					
Magnesium							
Magnesium chloride							2800
Magnesium hydroxide							
Magnesium perchlorate							
Magnesium sulfate							
Malathion		0.09/4h *		6/6h *	M: 471		290
Maleic acid							708
Maleic anhydride							481
Maleic hydrazide							3800
Malononitrile							61
Maneb							4500
Mannitol							17000
MCPA					M: 814		700
MCPB							700
Melamine							3161
Mephosfolan							9
Mercaptobenzothiazole							1680
Mercaptodimethur							60
Mercuric acetate							40.9
Mercuric ammonium chloride							
Mercuric chloride					29		1
Mercuric cyanide							
Mercuric iodide					M: 357		40
Mercuric nitrate							26
Mercuric oxide							18
Mercuric sulfate							57
Mercuric sulfide							
Mercuric thiocyanate							46
Mercurous chloride							166
Mercurous nitrate							170
Mercury							
Mercury fulminate							

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Mesityl oxide				2205/4h *			1120
Mesitylene				5/4h *			
Methacrylamide							459
Methacrylic anhydride							
Methacrylonitrile				328/4h			120
Methacryloyl chloride				14/4h *			
Methallyl chloride	22000/10m			9031/30m *			
Methane							
Methanesulfonyl fluoride							2
Methidathion				286/4h *			20
Methiocarb							15
Methoxychlor							5000
Methoxyethylmercuric acetate					6430		22
Methyl 2-chloroacrylate							
Methyl acetate		32000/4h					6970
Methyl acetylene							
Methyl acrylate		1000/4h		1350/4h			277
Methyl alcohol				64000/4h	143 - 428		5628
Methyl amyl acetate							6160
Methyl amyl alcohol		2000/4h					2590
Methyl bromide	M: 60000/	3120/15m		302/8h			214
Methyl butyl ether							
Methyl butyl ketone				8000/4h			2590
Methyl chloride	20000/2h			2525/4h *			1800
Methyl chloroformate				88/1h			60
Methyl disulfide				15.9mg/m3/2h			
Methyl ethyl ketone		2000/4h		7838/8h *			2737
Methyl ethyl ketone peroxide				200/4h			484
Methyl ethyl phenol methyl carbamate							
Methyl ethyl pyridine		1000/4h					368
Methyl formate							1622
Methyl hexyl ketone							
Methyl isobutyl ketone		4000/4h					2080
Methyl isocyanate				5/4h			51.5
Methyl isopropenyl ketone		125/4h					180
Methyl isothiocyanate					F: 1000		97
Methyl mercaptan				675			
Methyl methacrylate				3750			7872
Methyl parathion				3.5/4h *			6.01
Methyl phencapton							2.2
Methyl salicylate					506		887
Methyl thiocyanate							60
Methyl trichlorosilane							31
Methyl vinyl ketone				2.4/4h *			
Methylamine							100 - 200
Methylaniline							
Methylcyclopentadienyl manganese tricarbonyl				8.4/4h *			50
Methylcyclopentane							
Methyldichlorosilane		300/4h					
Methylene chloride				24924/30m	357		1600

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Methylethanolamine							2340
Methylhydrazine				74/4h			33
Methylmercuric dicyanamide							
Methylpyrrolidone							3914
Methylstyrene							4000
Methylthiouracil							2790
Methyltrichlorosilane		450/4h		400/4h			30
Methyomyl							
Metobromuron							2000
Metolcarb							
Mevinphos				14/1h			
Mexacarbate							14
Molybdenum tioxide							125
Monocrotophos				6.8/4h *			8
Morpholine				8000/8h			1050
MTBA							
N,N'-Diethylhydrazine							
N,N-Diethyl-p-phenylenediamine							
N,N-Dimethylaniline					50		1410
N-(4-Ethoxyphenyl) acetamide							1500
N-(Aminothioxomethyl) acetamide							
N-9H-Fluorenyl acetamide							
N-Butyl-N-nitroso-1-butanamine							1200
N-Ethyl-N-nitroso carbamide							300
N-Ethyl-N-nitroso ethanamine							280
N-Nitrosodiphenylamine							1650
N-Nitrosomorpholine							282
N-Nitrosopiperidine							200
N-Nitrosopyrrolidine							900
Nabam							395
Naled				7.7			250
Naphtha	30000/5m						
Naphthalene					C: 100		490
Neohexane							
Neopentyl glycol							
Nickel acetate							350
Nickel ammonium sulfate							400
Nickel bromide							
Nickel carbonyl	30/30m			35/30m			
Nickel chloride							175
Nickel cyanide							
Nickel fluoborate							
Nickel formate							
Nickel hydroxide							1500
Nickel nitrate							
Nickel sulfate							
Nicotine sulfate				1.3 *			50
Nitralin							> 2000
Nitric acid							
Nitric oxide				656 *	430		

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Nitrilotriacetic acid							1100
Nitroanaline							750
Nitrobenzene							640
Nitroethane							1100
Nitrofen							740
Nitrogen (liquefied)							
Nitrogen dioxide	200/1h			88/4h			
Nitrogen tetroxide							
Nitroglycerin							525
Nitromethane							940
Nitrophenol							250
Nitropropane				3100/8h			455
Nitrosodimethylamine				78/4h	F: 20		58
Nitrosoguanidine							
Nitrosyl chloride							
Nitrotoluene							1072
Nitrous oxide				584/4h *			
Nonane				3200/4h			
Nonanoic acid							
Nonanol							3200 - 6400
Nonene							
Nonylphenol							1620
Norbormide							
Octachloronaphthalene							
Octamethyl pyrophosphoramide							
Octane							
Octanol							> 3200
Octene							
Octyl aldehyde							5630
Oleic acid							74000
Oleum	347/1h						
Oxalic acid							375
Oxydisulfoton							
Oxygen (liquefied)							
p-Chloroaniline							310
p-Chlorophenol							261
p-Cresidine							1450
p-Cymene		5000/45m					4750
p-Dichlorobenzene							500
p-Dioxane	470/3d			12557/2h *			5170
p-Nitrosodiphenylamine							
p-Phenylenediamine							147
Paraldehyde							1530
Paraquat					214		57
Paraquat dimethylsulfate							320
Parathion				7/4h *	0.171 - 3.0		2
PCBs							845 - 16000
Pentaborane							
Pentachlorobenzene							1080
Pentachloroethane							

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Pentachloronitrobenzene							> 12000
Pentachlorophenol				32 *	401		27
Pentadecanol							
Pentadecylamine				95/4h *			660
Pentaerythritol							
Pentane							
Pentene							
Peracetic acid							
Perchloric acid							1100
Perchloromethyl mercaptan							82.6
Phenanthrene							
Phenol					140 - 14000		317
Phenyl mercuric acetate							22
Phenyldichloroarsine							
Phenylhydrazine hydrochloride				316 mg/m3			
Phenylsilatrane							
Phenylthiourea							3
Phorate				1/1h *			1
Phosacetim							
Phosfolan							
Phosgene	50/5m		803 *	50/30m			
Phosmet							300
Phosphamidon							20 - 22.4
Phosphine							
Phosphoric acid							1530
Phosphorus oxychloride				32/4h			380
Phosphorus pentasulfide							389
Phosphorus pentoxide				206/1h *			
Phosphorus red							
Phosphorus tribromide							
Phosphorus trichloride				104/4h			580
Phosphorus white					1.4		3.03
Phthalic acid							
Phthalic anhydride							4020
Picloram							2898
Picric acid							
Piperazine							1900
Piperidine							
Polyaromatic hydrocarbons							
Polyphosphoric acid							
Potassium							
Potassium aluminate							
Potassium arsenate							
Potassium arsenite							14
Potassium binoxalate							
Potassium bromate							321
Potassium carbonate							1870
Potassium chlorate							1870
Potassium chloride					M: 20		2600
Potassium chromate							

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Potassium cyanide					2.857		5
Potassium dichloroisocyanurate							
Potassium dichromate					C: 26		
Potassium fluoride							245
Potassium hydroxide							273
Potassium iodide							
Potassium metabisulfite							
Potassium nitrate							3750
Potassium oxalate							
Potassium permanganate					143		1090
Potassium peroxide							
Potassium silver cyanide							
Potassium sorbate							4340
Potassium sulfate							
Promecarb							
Propane							
Propanolamine							2830
Propargite							1480
Propargyl alcohol							20
Propargyl bromide							
Propiolactone				25/6h			
Propionaldehyde							1410
Propionic acid							2600
Propionic anhydride							2360
Propionitrile							39
Propoxur							95 - 104
Propyl acetate							9370
Propyl alcohol					F: 5700		1870
Propyl chloroformate							
Propyl mercaptan				7300/4h			1790
Propylamine							2310
Propylene							
Propylene chlorohydrin							
Propylene glycol							20000
Propylene glycol methyl ether							5860
Propylene glycol, allyl ether							
Propylene oxide				7200/1h			380
Propyleneimine							19
Prothoate							
Pseudocumene				3.6/4h *			5000
Pyrene				20			2700
Pyridine							891
Pyrocatechol							260
Pyrogallic acid					28		789
Quinoline							331
Quinone							130
Resorcinol					29		301
Rotenone					143		60
Salicylic acid							891
Sarin							

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Selenium dioxide							
Selenium disulfide							
Selenium oxychloride							
Selenium trioxide							50
Selenourea							
Selenous acid							
Semicarbazide hydrochloride							
Silicon tetrachloride							
Silver acetate							
Silver carbonate							
Silver cyanide							123
Silver fluoride							
Silver iodate							
Silver nitrate							
Silver oxide							
Silver sulfate							
Sodium							
Sodium acetate							3530
Sodium aluminate							
Sodium amide							
Sodium anthraquinone sulfate							
Sodium arsenate							< 50
Sodium arsenite					C: 2		41
Sodium azide					143		27
Sodium benzoate							4070
Sodium bicarbonate							4220
Sodium bifluoride							
Sodium bisulfate							2000
Sodium bisulfite							2000
Sodium borate					M: 709		2660
Sodium borohydrite							
Sodium bromide							3500
Sodium cacodylate							2600
Sodium carbonate				522/2h *			4090
Sodium chlorate							1200
Sodium chloride							3000
Sodium chlorite							165
Sodium chromate							
Sodium cyanide					2.857		6.44
Sodium dichloroisocyanurate					3570		1400
Sodium dichromate							50
Sodium ferrocyanide							
Sodium fluoaluminate							
Sodium fluoride					71 - 75		52
Sodium fluoroacetate					0.714		0.1
Sodium fluorosilicate							125
Sodium formate							
Sodium hydride							
Sodium hydrosulfite							
Sodium hydroxide							

TABLE A6 — MAMMALIAN TOXICITIES

Notes: m: minutes h: hours d: days w: weeks

C: child M: male F: female

Chemical	INHALATION LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	ORAL LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Sodium hypochlorite							
Sodium metabisulfite							
Sodium methanearsonate							
Sodium methylate							
Sodium nitrate					114		3236
Sodium nitrilotriacetic acid							
Sodium nitrite							85
Sodium oxalate							
Sodium pentachlorophenate							
Sodium perchlorate							2100
Sodium phosphate, dibasic							17000
Sodium phosphate, monobasic							8290
Sodium phosphate, tribasic							7400
Sodium phosphide							
Sodium selenite							7
Sodium silicate							1153
Sodium sulfate							
Sodium sulfide							
Sodium sulfite							
Sodium thiocyanate							764
Sodium thioglycolate							
Sodium thiosulfate							
Sodium tripolyphosphate							4000
Sorbic acid							7360
Sorbitol							15900
Stannic chloride				212/10m *			
Stannous chloride							700
Strontium							
Strontium chromate							3118
Strontium nitrate							2750
Strontium sulfide							
Strychnine					30		2.35
Strychnine sulfate							2.6
Styrene							1000
Styrene oxide							
Sulfamic acid							3160
Sulfolane							1941
Sulfotepp							
Sulfur							
Sulfur chloride							
Sulfur dioxide	1000/10m			2520/1h			
Sulfur tetrafluoride							
Sulfur trioxide							
Sulfuric acid	0.7/24w *			125/2h *			2140
Sulfuryl chloride							
Sulfuryl fluoride							100
Tabun							
Tall oil							
Tannic acid							2260
Tartaric acid							

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
TCDD							22500
Tebuthiuron							644
Tellurium hexafluoride							
Temephos							8600
Terephthalic acid							> 6400
Terphenyl							
Tetrabutyl titanate							3122
Tetrachloroethane							800
Tetrachloroethylene	M: 2857			4932/8h *			2629
Tetrachlorvinphos							
Tetradecanol							
Tetradecene							
Tetradecylbenzene							
Tetraethyl lead				63/1h *			35
Tetraethyl pyrophosphate							1.12
Tetraethylene glycol							29000
Tetraethylenepentamine							3990
Tetraethyltin							16
Tetrafluoroethylene							
Tetrahydrofuran				21000/3h			2816
Tetrahydronaphthalene							2860
Tetramethyl lead				810/1h *			109
Tetranitromethane				18/4h			130
Tetrasodium pyrophosphate							4000
Thallic peroxide							
Thallium							
Thallium acetate					12		41.3
Thallium chloride							
Thallium nitrate							
Thallium sulfate					2.166		16
Thallium(I) carbonate							
Thioglycolic acid							114
Thiometon							100 - 120
Thionazin							
Thionyl chloride							
Thiophan sulfone							1941
Thiophenol				33/4h			46.2
Thiophosgene							929
Thiosemicarbazide							9.16
Thiourea							125
Thiram				49/4h *			560
Thorium dioxide							
Thorium nitrate							
Titanium dioxide							
Titanium tetrachloride							
Toluene				51 *	50		5000
Toluene-2,4-diamine							260
Toluene-2,4-diisocyanate				14/4h			5800
Toluenesulfonic acid							2400
Toluidine							656

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Chemical							
Tolyl thiourea							
Toxaphene					40		40
Tri(2-butoxyethyl) phosphate							3000
Tri-o-cresyl phosphate							3000
Triallate							1471
Triamiphos							
Tributyl phosphate							3000
Trichloro triazine							
Trichloroacetaldehyde					4		479
Trichloroacetyl chloride				63/4h *			600
Trichlorobenzene							756
Trichlorocyanuric acid					3570		406
Trichloroethane	4869/10m *			18000/4h			10300
Trichloroethyl amine							
Trichloroethylene				8000/4h	7000		4920
Trichlorofluoromethane				130000/15m			
Trichlorofon				1215 *			150
Trichloronate							
Trichlorophenol							820
Trichlorophenoxy propionic acid							650
Trichlorophenyl silane							
Trichlorosilane							1030
Trichlorotrifluoroethane				11000/2h			43000
Tridecene							
Tridecyl alcohol							17200
Triethanolamine							8000
Triethoxysilane				45/2h *			
Triethylaluminum				2107/15m *			
Triethylamine							460
Triethylbenzene							
Triethylene glycol					5000		22060
Triethylene tetramine							2500
Trifluorochloroethylene				1000/4h			
Trifluralin							
Triisobutylaluminum							> 10000
Trimellitic anhydride							5600
Trimethylamine							
Trimethylchlorosilane							
Trimethylene bromide							1373
Trimethylene chloride							
Trinitrobenzene							450
Trinitrotoluene							820
Triphenyltin chloride							135
Tripropylene glycol							3000
Tris(1-aziridinyl) phosphine oxide							37
Trisodium nitrilotriacetate							1100
Turpentine							5760
Undecanol							3000
Undecylbenzene							
Uranium dioxide							

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Uranium hexafluoride							
Uranyl acetate							
Uranyl nitrate							
Uranyl sulfate							
Urea							8471
Urea peroxide							
Urethan							
Valeraldehyde							4581
Vanadium oxide							
Vanadium oxytrichloride							140
Vanadium pentoxide							10
Vanadyl sulfate							
Vinyl acetate				4000/2h			2920
Vinyl bromide							500
Vinyl chloride							
Vinyl fluoride							
Vinyl methyl ether							4900
Vinyl styrene							
Vinylidene chloride							
Vinylnorbornene							4365
Vinyltrichlorosilane							1280
Warfarin				25 *	6.667		1.6
Xylene	10000/6h			5000/4h	50		4300
Xylenol							296
Zinc acetate							794
Zinc ammonium chloride							
Zinc arsenate							
Zinc borate							
Zinc bromide							
Zinc carbonate							
Zinc chloride							350
Zinc chromate							
Zinc cyanide							1400
Zinc fluoborate							
Zinc fluoride							
Zinc formate							
Zinc hydrosulfite							
Zinc nitrate							1190
Zinc oxide					500		
Zinc phenolsulfonate							
Zinc phosphate							
Zinc phosphide					80		40
Zinc silicofluoride							
Zinc stearate							
Zinc sulfate							2150
Zirconium acetate							
Zirconium nitrate							2290
Zirconium oxychloride							
Zirconium potassium fluoride							
Zirconium sulfate							3500

TABLE A6	MAMMALIAN TOXICITIES						
Note: m: minutes h: hours d: days w: weeks	INHALATION				ORAL		
C: child M: male F: female Chemical	LCLo (human) (ppm)	LCLo (rat) (ppm)	LC50 (human) (ppm)	LC50 (rat) (ppm)	LDLo (human) (mg/kg)	LD50 (human) (mg/kg)	LD50 (rat) (mg/kg)
Zirconium tetrachloride							1688
1,1-Dichloropropene							6500
1,2,4,5-Tetrachlorobenzene							1500
1,2-Benzisothiazolin-3-one 1,1-dioxide							
1,2-Dibromo-3-chloropropane				103/8h			170
1,2-Dihydro-3-methyl benz[j]aceanthrylene							
1,2-Diphenylhydrazine							
1,2-Ethanediylbiscarbamodithioic acid							
1,2-Methylenedioxy-4-allyl benzene							
1,2-Methylenedioxy-4-propenyl benzene							
1,2-Methylenedioxy-4-propyl benzene							
1,2-Oxathiolane-2,2-dioxide							
1,2:7,8-Dibenzopyrene							
1,3-Butanediol							23000
1,4-Dichloro-2-butene	86/4h	62/4h					
1,4-Naphthalenedione							190
1-(Chloromethyl)-4-nitrobenzene							
1-Amino-2-methyl anthraquinone							
1-Bromo-4-phenoxy benzene							
1-Chloronaphthalene							1540
1-Naphthol							2400
1-Naphthylamine							8400
10,10'-Oxydiphenoxarsine							
2,2'-Thiobis(4,6-dichlorophenol)							7
2,2'-Thiobis[4-chloro-6-methyl] phenol							
2,3,4,6-Tetrachlorophenol							140
2,3-Dibromo-1-propanol phosphate							1010
2,3-Dichloropropene							320
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)							300
2,4,6-Trimethyl aniline							743
2,4-Dichlorophenol							580
2,4-Dichlorophenoxyacetic acid (2,4-D)					80		370
2,4-Dinitrophenol					4.3		30
2,4-Dinitrotoluene							268
2,6-Dinitrophenol							
2,6-Xylidine							130
2-Aminoanthraquinone							
2-Chlorophenyl thiourea							4.6
2-Methyl benzenamine hydrochloride							2951
2-Methyl-5-vinyl pyridine							
2-Naphthol							1960
2-Naphthylamine							727
2-Phenylphenol							2000
2-Picoline							
3,3'-Dichloro(1,1'-biphenyl)-4,4'-diamine							7070
3,3'-Dimethylbiphenyl-4,4'-diamine							404
3,4-Dichlorophenyl isocyanate				18/2h *			
3,4-Dinitrotoluene							177
3-(Trifluoromethyl) benzenamine				58/4h *			480
3-Chloropropionitrile							100

TABLE A6	MAMMALIAN TOXICITIES						
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Chemical							
3-(p-Di(chloroethyl)amino) phenyl-L-alanine							
4'-Amino propiophenone							
4,4'-Diaminodiphenyl ether							
4,4'-Methylene dianiline							725
4,4'-Methylenebis(2-chloro) anilene							
4,4'-Thiodianiline							1100
4,5-Dichloro-2-trifluoromethyl benzimidazole							
4,6-Dinitro-o-cyclohexylphenol							65
4-Aminoazobenzene							
4-Aminobiphenyl							500
4-Aminobutyl diethoxymethyl silane							
4-Aminopyridine					0.59		21
4-Chlorobenzenamine							310
4-Chlorophenyl phenyl ether							
4-Nitrobiphenyl							2230
5-chloro-2-(2,4-dichlorophenoxy) phenol							
5-Nitro-o-anisidine							
5-(Bis(2-chloroethyl)amino) uracil							7.5
7,12-Dimethyl-1,2-benzanthracene							327

* : Values have been converted from mg/m3 to ppm using the following formula:
: x ppm = (24.054/mol wgt) X y mg/m3